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REARRANGEMENT OF HYDROCARBON CARBANIONS

A THESIS

Presented to

the Faculty of the Graduate Division

by

Laney Peter Williams, Jr.

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in the School of Chemistry

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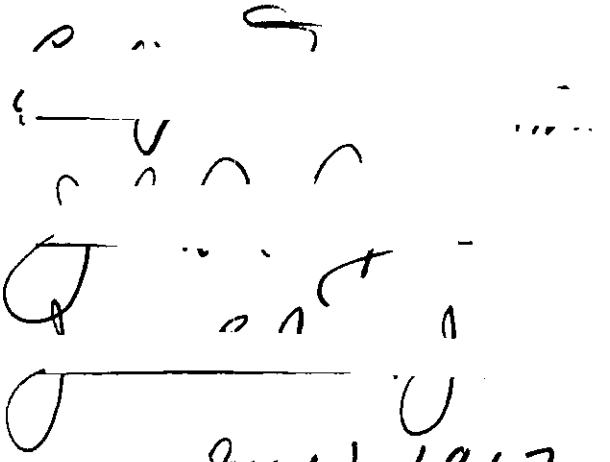
June, 1962

REARRANGEMENT OF HYDROCARBON CARBANIONS

Approved:



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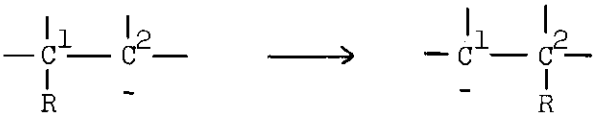
SUMMARY

The purpose of this research was to study under what conditions of structure and environment molecular rearrangements of carbon skeleton involving 1,2-shifts in carbanions may be realized. This type of carbanion rearrangement may be summarized as:



This was of interest because the number of cases in which a carbanion, containing only carbon and hydrogen near the reaction center, is known to undergo 1,2-shift of carbon skeleton is very small.

In the first part of this research, the 2,2,2-triphenylethyl carbanion was generated by reaction of 2-chloro-1,1,1-triphenylethane with an alkali metal and the extent of rearrangement under varying conditions was determined. The products from these reactions were analyzed after preliminary reaction with carbon dioxide to convert the organoalkali compounds to carboxylic acids. These acids were analyzed by a variety of techniques depending on their composition. The techniques used most often were silicic acid chromatography, quantitative infrared spectral analysis, and vapor-phase chromatography. The hydrocarbons which always accompanied the acids were separated and sometimes analyzed by similar techniques.

The reaction of 2-chloro-1,1,1-triphenylethane with potassium in refluxing tetrahydrofuran, followed by carbonation, gave as high as 72 per cent yields of 2,2,3-triphenylpropanoic acid. This acid results from

the rearranged organopotassium compound, 1,1,2-triphenylethylpotassium. No evidence for the unrearranged 2,2,2-triphenylethylpotassium was found at temperatures of -50 to 66° using tetrahydrofuran or 1,2-dimethoxyethane as solvent. Therefore, potassium reacts with 2-chloro-1,1,1-triphenylethane to give 1,1,2-triphenylethylpotassium but no detectable 2,2,2-triphenylethylpotassium under the conditions studied.

However, 2-chloro-1,1,1-triphenylethane has been found to react with lithium in tetrahydrofuran to give 2,2,2-triphenylethyllithium which is comparatively stable at temperatures from -65 to -30° but readily undergoes rearrangement at temperatures of 0° or higher to give 1,1,2-triphenylethyllithium. These results lend considerable support to the supposition that this rearrangement occurs by way of an intermediate carbanion and none to the supposition that it occurs by way of a free-radical intermediate. If the rearrangement occurs via an intermediate carbanion, then the extent of rearrangement should decrease in going along the series of alkali metals in the order, K > Na > Li, since the organolithium compound would have the most and the organopotassium compound the least covalent character in the carbon-metal bond. Alternately, if the rearrangement occurs via a free-radical intermediate, then lithium should give the most and potassium the least rearrangement in conformity with the better reducing power of potassium which should give a lower concentration of free radicals.

In the second part of this research, the effect of structure upon the extent of occurrence of carbanion rearrangements and upon the ease of migration of various groups was studied. The reaction of 1-chloro-2,2,3-triphenylpropane with lithium in tetrahydrofuran has been found to give

2,2,3-triphenylpropyllithium, which is comparatively stable at -65°, but when warmed to 0° it rapidly rearranges to give 1,1,3-triphenylpropyllithium. Two aspects of this rearrangement are especially interesting. In the first place, only benzyl migration was noted. No products corresponding to phenyl migration were isolated. Also, by comparing the above rearrangement to that of 2,2,2-triphenylethyllithium under identical conditions it was found that benzyl migration occurs at a considerably faster rate than phenyl migration. This demonstrates the superior intrinsic migratory aptitude of benzyl over phenyl in the present rearrangement. Since a greater migratory aptitude of benzyl over phenyl has also been noted in Wittig rearrangements, a related carbanion rearrangement, this is additional evidence in support of a carbanion mechanism for the present rearrangement.

The reaction of 1-chloro-2-methyl-2-phenylpropane with lithium in tetrahydrofuran at -65° has been found to give 2-methyl-2-phenylpropyllithium, which is fairly stable at that temperature. However, it is only moderately stable at 0° and is completely decomposed in four hours at 30°. No evidence for either of the organolithium compounds which would result from methyl or phenyl migration was found in the acidic products. In the neutral products, a small amount of one or both of the hydrocarbons which would result from the rearranged organolithium is found but the major hydrocarbon found results from the unrearranged organolithium compound. Therefore, the 2-methyl-2-phenylpropyllithium apparently is decomposed (protonated by the solvent) much faster than it rearranges. This lack of rearrangement indicates that steric strain may be an important factor in determining whether an organometallic compound will undergo rearrangement.

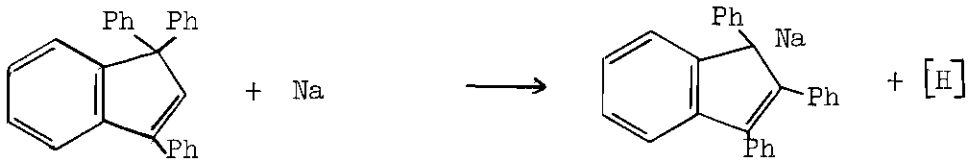
The 2-methyl-2-phenylpropyllithium may have a lack of steric strain since it has only one large substituent on the beta-carbon. Thus far, all of the hydrocarbon carbanions which have been found to undergo rearrangement have had a quaternary carbon bearing two or three large substituents, which was converted by rearrangement into a trigonal carbon bearing one less large substituent.

CHAPTER I

INTRODUCTION

The purpose of this research was to study under what conditions of structure and environment molecular rearrangements of carbon skeleton involving 1,2-shifts in carbanions may be realized. This type of carbanion rearrangement may be summarized as:

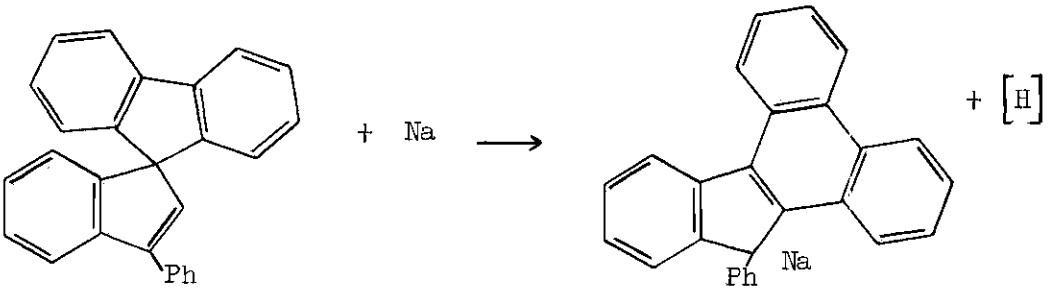
A number of rearrangements of carbanions involving rearrangement of carbon skeleton have been studied which seem to depend upon the presence of an electronegative atom such as tetravalent nitrogen, trivalent sulfur, or divalent oxygen one atom removed from the center of carbanion formation. The Stevens rearrangement of quaternary ammonium salts and the Wittig rearrangement of others are examples of this type of rearrangement.[1] The number of cases in which a carbanion containing only carbon and hydrogen near the reaction center undergoes 1,2-shift of carbon skeleton is very small. Some possible examples are the reaction of 1,1,3-triphenylindene[2] with sodium to give



(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 523-528 and 642-644.

(2) K. Ziegler and K. Bahr, Ber., 61, 253 (1928).

the sodium derivative of 1,2,3-triphenylindene and the similar rearrangement of 1-biphenylene-3-phenylindene.[3]



In another example, Wooster and Mitchell[4] reported that when the compound to which Cone and Robinson[5] had assigned the structure of 2-chloro-1,1,1-triphenylethane was treated with sodium in liquid ammonia, a red organosodium compound was obtained which upon treatment with ammonium chloride gave 1,1,2-triphenylethane. Wooster and Mitchell accordingly concluded that a rearrangement of carbon skeleton had occurred during the reaction with sodium; however the compound of Cone and Robinson has been shown by Grovenstein[6] and by Charlton, Dostrovsky and Hughes[7] to be 2-chloro-1,1,2-triphenylethene and thus no rearrangement of carbon skeleton need be postulated. Also when authentic 2-chloro-1,1,1-triphenylethane was reacted[7] with sodium in liquid ammonia followed by treatment with ammonium chloride 1,1,1-triphenylethane resulted. However the

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(3) C. F. Koelsch, J. Am. Chem. Soc., 55, 3394 (1933); 56, 480 (1934).

(4) C. B. Wooster and N. W. Mitchell, J. Am. Chem. Soc., 52, 1042 (1930).

(5) L. H. Cone and C. S. Robinson, Ber., 40, 2164 (1907).

(6) E. Grovenstein, Jr., J. Am. Chem. Soc., 79, 4985 (1957).

(7) J. C. Charlton, I. Dostrovsky and E. D. Hughes, Nature, 167 986 (1951).

reaction of 2-chloro-1,1,1-triphenylethane with sodium in refluxing dioxane[6] gives a red organosodium compound which undergoes carbonation to give 2,2,3-triphenylpropanoic acid:

$$Ph_3CCH_2Cl \xrightarrow[\text{dioxane}]{Na} Ph_2\underset{Na^+}{C^-}CH_2Ph \xrightarrow{CO_2} Ph_2\underset{CO_2H}{C}CH_2Ph$$

Zimmerman and Smentowski[8] obtained the same results when the reaction was run in ethyl ether-isooctane at room temperature. In a similar reaction[6] but with t-amyl alcohol added to the dioxane used as solvent, the hydrocarbon product consisted of 94 per cent 1,1,1-triphenylethane and 6 per cent 1,1,2-triphenylethane; thus t-amyl alcohol donates a proton (apparently to a reactive intermediate such as Ph_3CCH_2Na) before rearrangement occurs. Triphenylethylene, which results from the pyrolysis[7] of 2-chloro-1,1,1-triphenylethane alone but especially in the presence of ferric and stannic chloride, cannot be an important intermediate in the reaction with sodium since this compound gives rise to different products from those obtained from 2-chloro-1,1,1-triphenylethane upon reaction with sodium in dioxane followed by carbonation. The different products[6] consist of an incompletely identified mixture of carboxylic acids whose neutralization equivalent shows approximately two carboxyl groups per triphenylethylene and which in part undergoes dehydration to give triphenylsuccinic anhydride.

In the reactions cited above, the evidence seems to point to phenyl migration occurring by way of an intermediate carbanion, the 2,2,2,-tri-

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(8) H. E. Zimmerman and F. J. Smentowski, J. Am. Chem. Soc., 79, 5455 (1957).

phenylethyl carbanion. However rearrangement by way of an intermediate 2,2,2-triphenylethyl radical could also account for the products since phenyl groups are known to migrate in free-radical reactions and the 2,2,2-triphenylethyl radical was 100 per cent rearranged under the conditions of Curtin and Hurwitz.[9] Therefore one objective of this research was to find out whether any rearrangements of hydrocarbon carbanions do occur or whether all such apparent rearrangements are actually only rearrangements of free radicals.

In the first part of this research, the 2,2,2-triphenylethyl carbanion was generated by reaction of 2-chloro-1,1,1-triphenylethane with an alkali metal and the extent of rearrangement determined. Where feasible the reaction was run over a wide range of temperature and in several different solvents or mixtures of solvents. Since the effect upon the extent of rearrangement of varying the alkali metal should tell something about the nature of the step involved in the rearrangement, the effect of treating the 2-chloro-1,1,1-triphenylethane with potassium, sodium-potassium alloy, and lithium was studied. The products from all these reactions were analyzed after preliminary reaction with carbon dioxide to convert the organoalkali compounds to carboxylic acids. These acids were analyzed by a variety of techniques depending on their composition. The techniques used most often were silicic acid chromatography, quantitative infrared spectral analysis, and vapor-phase chromatography. The hydrocarbons which always accompanied the acids were separated and sometimes analyzed by similar techniques.

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(9) D. Y. Curtin and M. J. Hurwitz, J. Am. Chem. Soc., 74, 5381 (1952).

In the second part of this research, the effect of structure upon the extent of occurrence of carbanion rearrangements and upon the ease of migration of various groups was studied. The carbanions chosen for study were the 2,2,3-triphenylpropyl carbanion and the 2-methyl-2-phenylpropyl carbanion. In these carbanions the methyl and benzyl groups are pitted against the phenyl group for rearrangement. Since the ease of migration for these groups is different in free-radical rearrangements and carbanion rearrangements, the ease of migration found in this study should be indicative of the mechanism. These carbanions will be generated from 1-chloro-2,2,3-triphenylpropane and 1-chloro-2-methyl-2-phenylpropane by reaction with lithium and analyzed by the techniques mentioned above.

CHAPTER II

DISCUSSION OF EXPERIMENTAL RESULTS

Reaction of 2-Chloro-1,1,1-triphenylethane with Potassium and Sodium-potassium Alloy.--The reaction of 2-chloro-1,1,1-triphenylethane with molten potassium in refluxing tetrahydrofuran (b.p. 65-66°) gave a very dark red solution which upon carbonation gave some 72 per cent yield of 2,2,3-triphenylpropanoic acid and 4.7 per cent of diphenylacetic acid. The major acidic product was therefore identical with that obtained from reaction with molten sodium in refluxing dioxane[6] except for a higher yield (43 per cent yield of 2,2,3-triphenylpropanoic acid reported with sodium in dioxane). The diphenylacetic acid probably comes from diphenylmethylpotassium which could result from cleavage of a carbon-carbon bond of some intermediate product by potassium. The intermediate product undergoing cleavage by potassium is not known with certainty but 1,1,2-triphenylethane, which has been identified in the corresponding reaction with sodium,[6] is a very likely possibility. It is known that 1,1,2,2-tetraphenylethane is cleaved by sodium-potassium alloy to diphenylmethylpotassium,[10,11] 1,1,1,2-tetraphenylethane is similarly cleaved to triphenylmethylpotassium,[10] while 1,2-diphenylethane is not cleaved.[11] Recently Rogers[12] has found that 1,1,2-triphenylethylene is cleaved by sodium in liquid ammonia to diphenylmethane and toluene.

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(10) K. Ziegler and F. Thielmann, Ber., 56B, 1743 (1923).

(11) J. B. Conant and B. S. Garvey, J. Am. Chem. Soc., 49, 2599 (1927).

(12) L. C. Rogers, private communication.

Further reactions of 2-chloro-1,1,1-triphenylethane with potassium were carried out at lower temperatures to see if the reaction proceeded with rearrangement at these temperatures also. The reaction was studied with liquid sodium-potassium alloy in tetrahydrofuran at 20 and 0° and gave, respectively, 53 and 32 per cent yields of 2,2,3-triphenylpropanoic acid and 1 and 0 per cent yields of diphenylacetic acid. Attempts were made to study the reaction of 2-chloro-1,1,1-triphenylethane with finely divided potassium at -10 and -78°. These reactions failed because of agglomeration of the potassium under all conditions studied where the surface of the potassium was clean enough to permit reaction. Although blue solutions due to solubility of potassium in tetrahydrofuran have been reported,[4] no blue solutions of tetrahydrofuran were noted in any of the experiments carried out in this research. However the report[13] that a blue solution is formed by potassium in 1,2-dimethyoxyethane at temperatures near the freezing point of the solvent was confirmed in this research. In experiments at -50° with a finely divided suspension of potassium in 1,2-dimethoxyethane a deep blue color was noted. The addition of a small amount of 2-chloro-1,1,1-triphenylethane would discharge this color and give the usual red-brown color of the organopotassium compound. The deep blue color would return to the solution upon additional stirring at this temperature. A small amount of 2-chloro-1,1,1-triphenylethane was reacted with potassium at -50° before the reaction was terminated due to agglomeration of the potassium. Carbonation of this reaction mixture gave a mixture which contained only 2,2,3-triphenylpropanoic acid and

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(13) J. L. Down, J. Lewis, B. Moore and G. Wilkinson, Proc. Chem. Soc., 209 (1957).

triphenylsuccinic anhydride. The triphenylsuccinic anhydride probably resulted from carbonation of the addition product of potassium and triphenylethylene. Triphenylsuccinic acid has been shown[6] to be a product in the corresponding reaction of sodium and triphenylethylene. Triphenylethylene could be formed by alpha-elimination upon 2-chloro-1,1,1-triphenylethane by an organopotassium compound.[8]

Therefore potassium reacts with 2-chloro-1,1,1-triphenylethane at temperatures of from -50 to 66° to give 1,1,2-triphenylethylpotassium but no detectable 2,2,2-triphenylethylpotassium. Also the yields of the 1,1,2-triphenylethyl carbanion are generally higher with potassium than with sodium. These results lend support to the supposition that rearrangement in the reaction of 2-chloro-1,1,1-triphenylethane with alkali metals occurs by way of the 2,2,2-triphenylethyl carbanion since 2,2,2-triphenylpotassium would be expected to be more ionic in character[14] and therefore undergo rearrangement more readily than 2,2,2-triphenylethylsodium.

Reaction of 2-Chloro-1,1,1-triphenylethane with Lithium.--The reaction of lithium metal with 2-chloro-1,1,1-triphenylethane in tetrahydrofuran at -10° produced a deep red-colored solution. This solution was stirred at 28° for one hour and then carbonated. The resulting acids were separated by silicic acid chromatography and gave 18 per cent yield of 2,2,3-triphenylpropanoic acid and 10 per cent yield of triphenylsuccinic anhydride. The triphenylsuccinic anhydride probably resulted from carbonation of the addition product of lithium to triphenylethylene (in a similar

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(14) E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 65.

manner to that described previously with potassium). In partial confirmation of this a 5 per cent yield of triphenylethylene was found in the neutral products of this reaction.

Another reaction run at a temperature of -60° for 3-1/2 hours and than carbonated gave quite different results. This reaction gave 62 per cent yield of acids which consisted of 94 per cent 3,3,3-triphenylpropanoic acid, 3 per cent 2,2,3-triphenylpropanoic acid and 3 per cent triphenylsuccinic anhydride. Thus at -60° lithium reacts with 2-chloro-1,1,1-triphenylethane to give 2,2,2-triphenylethyllithium which is relatively stable at this temperature. Some or all of the 1,1,2-triphenylethyllithium (which upon carbonation gave the 3 per cent yield of 2,2,3-triphenylpropanoic acid) could have been formed when the reaction was initiated by addition of a small amount of the chloride at -10°. All of the reactions of 2-chloro-1,1,1-triphenylethane with lithium were initiated at -10° since several attempts to initiate reaction at lower temperatures failed. Apparently in the first experiment 2,2,2-triphenylethyllithium was formed initially but rapidly rearranged to 1,1,2-triphenyllithium at the higher temperature. In order to demonstrate that this was happening a reaction with lithium at -60° as described above was carried out and then warmed to 0° and stirred at this temperature for one hour before carbonation. The resulting acids yielded 30 per cent triphenylsuccinic anhydride, 44 per cent 2,2,3-triphenylpropanoic acid and 26 per cent 3,3,3-triphenylpropanoic acid. A second run under these conditions gave the same composition of acids within ± 5 per cent. Therefore at 0° approximately two-thirds of the 2,2,2-triphenylethyllithium underwent rearrangement to 1,1,2-triphenylethyllithium in one hour.

An attempt was made to increase the extent of rearrangement of 2,2,2-triphenyllithium by reacting it with a more reactive metal. A reaction was run at -60° and then warmed to 0° as before and then liquid sodium-potassium alloy was added and the reaction was stirred at 0° for one hour before carbonation. The resulting acids yielded 50 per cent triphenylsuccinic acid, 37 per cent 2,2,3-triphenylpropanoic acid and 13 per cent 3,3,3-triphenylpropanoic acid. This shows a small increase in the extent of rearrangement but the effect is not as pronounced as would be expected if the 2,2,2-triphenylethyllithium readily exchanged with potassium to give the more reactive 2,2,2-triphenylethylpotassium. Attempts were also made to accelerate the rearrangement of 2,2,2-triphenylethyllithium by increasing the solvating power of the medium for cations. A solution of 2,2,2-triphenylethyllithium was prepared at -60° in 200 ml. of tetrahydrofuran and then stirred at -60° for one hour after the addition of 100 ml. of triethylamine and carbonated. The resulting acid was essentially pure 3,3,3-triphenylpropanoic acid showing that the triethylamine had no appreciable effect. The ineffectiveness of triethylamine in promoting rearrangement can be understood in terms of a recent report[15] that triethylamine forms a considerably less stable complex with n-butyllithium in benzene than does tetrahydrofuran. This report is surprising since trimethylamine forms a considerably more stable coordination compound with trimethylaluminum than does dimethyl ether.[16] A number of attempts to study the reaction of 2-chloro-1,1,1-triphenylethane with lithium in

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(15) F. J. Welch, J. Am. Chem. Soc., 82, 6000 (1960).

(16) G. E. Coates, "Organo-metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 136.

1,2-dimethoxyethane were unsuccessful due to inability to effect reaction of the halide in this solvent.

Thus 2-chloro-1,1,1-triphenylethane has been found to react with lithium to give 2,2,2-triphenylethyllithium which is comparatively stable at temperatures from -65 to -30° but readily undergoes rearrangement at temperatures of 0° or higher to give 1,1,2-triphenylethyllithium. These results lend considerable support to the supposition that this rearrangement occurs by way of an intermediate carbanion and none to the supposition that it occurs by way of a free-radical intermediate. If the rearrangement occurs via an intermediate carbanion then the extent of rearrangement should decrease in going along the series of alkali metals in the order, K > Na > Li, since the organolithium compound would have the most and the organopotassium compound the least covalent character in the carbon-metal bond. Alternately, if the rearrangement occurs via a free-radical intermediate, then lithium should give the most and potassium the least rearrangement in conformity with the better reducing power of potassium which should give a lower concentration of free radicals.

Zimmerman and Zweig[17] have recently reported the rearrangement of 2,3-diphenylpropyllithium and of 2-phenyl-2-(p-tolyl)-propyllithium and conclude that these are rearrangements of carbanions on the basis of the greater extent of migration of phenyl rather than p-tolyl. They also observed that only rearranged potassium analogs could be obtained while magnesium analogs were immune to rearrangement.

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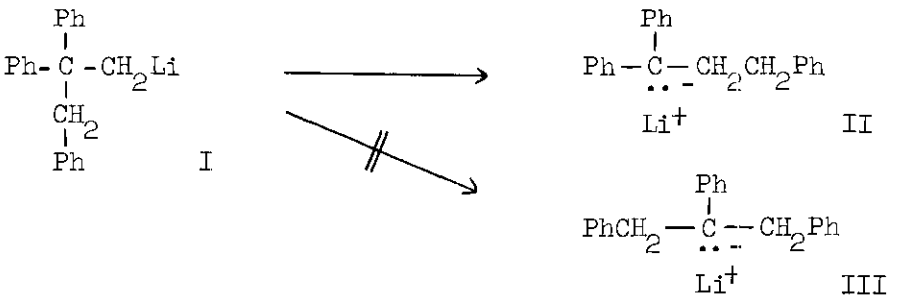
(17) H. E. Zimmerman and Z. Zweig, J. Am. Chem. Soc., 83, 1196 (1961).

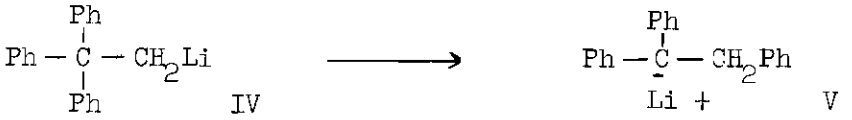
Reaction of 1-Chloro-2,2,3-triphenylpropane with Lithium.--1-Chloro-2,2,3-triphenylpropane was reacted with lithium metal in tetrahydrofuran at -65° for 3-1/2 hours before carbonation. The carboxylic acid which resulted was shown to be nearly pure 2,3,4-triphenylbutanoic acid and was obtained in 31 per cent yield. A similar reaction was carried out at -65° for 3-1/2 hours and was then warmed to 0° for one hour before carbonation. A 55 per cent yield of carboxylic acid resulted and this acid was shown to be nearly pure 2,2,4-triphenylbutanoic acid. A third reaction was carried out at -65° for 3-1/2 hours as before and then warmed to 0° for only 15 minutes before carbonation. The resulting 41 per cent yield of carboxylic acid was shown to be at least 98 per cent 2,2,4-triphenylbutanoic acid. Thus 1-chloro-2,2,3-triphenylpropane has been found to react with lithium to give 2,2,3-triphenylpropyllithium which is comparatively stable at -65° but when warmed to 0° rapidly rearranges to give 1,1,3-triphenylpropyllithium.



Two aspects of the above rearrangement are especially interesting. In the first place only benzyl migration was noted. Phenyl migration followed by carbonation would have given the known[18] 2,3-diphenyl-2-benzylpropanoic acid (m.p. 125-126°) of which no evidence was found in this work.

(18) K. Ziegler and B. Schnell, Ann., 437, 253 (1924).

Thus a benzyl group of 2,2,3-triphenylpropyllithium migrates more readily than a phenyl group. In the second place, I rearranges to II more readily than 2,2,2-triphenylethyllithium (IV) rearranges to 1,1,2-triphenylethyllithium (V) since at 0° only



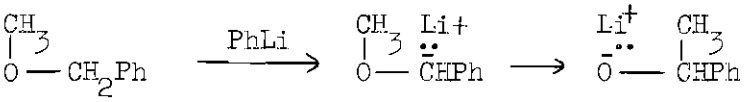
IV V

64 per cent of IV was rearranged to V in one hour but at 0° at least 98 per cent of I was rearranged to II in 15 minutes. This comparison of the rates of rearrangement of I and IV is of interest because of their close similarity in structure and the similarity of their products of rearrangement.

If one assumes that the rearrangement of I to II or III goes by way of rearrangement of a carbanion, then the rearrangement of I to II gives a carbanion which is stabilized by two alpha-phenyl groups but rearrangement of I to III gives a carbanion which is stabilized by only one alpha-phenyl group. If one also assumes that the transition states for these rearrangements have atomic and electronic configurations somewhere near midway between products and reactants, then the factors which contribute toward stabilization of the product will also stabilize the transition state. If this stabilization is the dominant factor in this rearrangement, then one would predict migration of benzyl over phenyl regardless of the relative migratory aptitudes of these groups. However, a comparison based on the rates of rearrangement of I and IV is made under more similar conditions since both rearrangements give carbanions of about equal stability; that benzyl migration occurs here at a considerably

faster rate than phenyl migration demonstrates the superior intrinsic migratory aptitude of benzyl over phenyl in the present rearrangement.

In the Wittig rearrangement of which a typical example[19] is:



a carbanion is converted into the less basic salt of an alcohol. In these rearrangements of carbanions, Wittig,[20] Curtin[21] and their co-workers observed the following order of decreasing ease of migration of groups as the group was varied: $CH_2{=}CHCH_2$, $PhCH_2$ > CH_3, CH_3CH_2 > Ph. For the rearrangement of free radicals the migratory aptitude of benzyl has apparently not been determined. One would suppose that the migratory aptitude of benzyl was less than that of phenyl for rearrangements of free radicals because radical displacements at a saturated carbon atom are very rare[22] while radical additions to aromatic rings are common. For the rearrangement of carbonium ions the following order of decreasing ease of migration of groups has been observed:[23] Ph > CH_3 > H > $PhCH_2$. Thus the migration of benzyl rather than phenyl in the rearrangement of 2,2,3-triphenylpropyllithium seems to be best explained as support for rearrangement by a carbanion mechanism.

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(19) G. Wittig and L. Lohman, Ann., 550, 260 (1942).

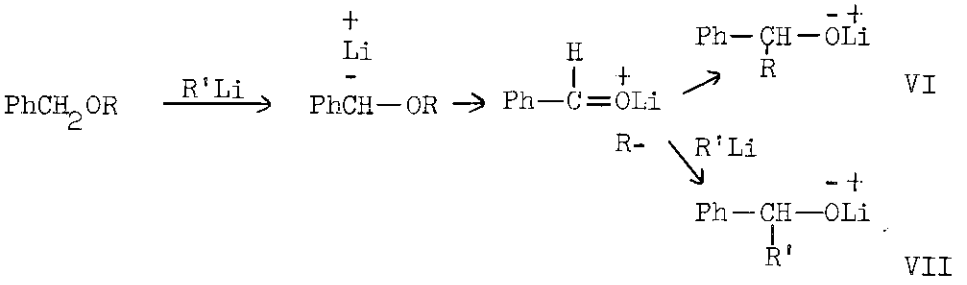
(20) G. Wittig, H. Doser and I. Lorenz, Ann., 562, 192 (1949).

(21) D. Y. Curtin and W. R. Proops, J. Am. Chem. Soc., 76, 494 (1954).

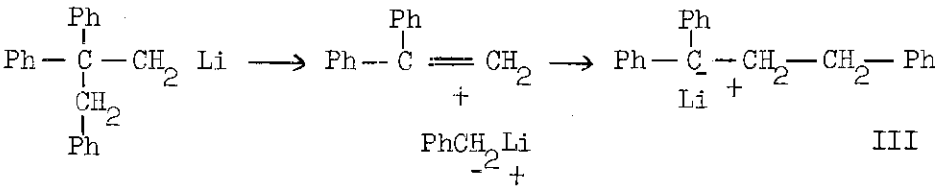
(22) R. A. Herrmann and R. M. Noyes, J. Am. Chem. Soc., 78, 5764 (1956).

(23) A. W. Fort and J. D. Roberts, J. Am. Chem. Soc., 78, 584 (1956).

The above argument is weakened somewhat by some recent work on the Wittig rearrangement. Schollkopf and Fabian[24] have reported extensive racemization in the rearrangement of optically active benzyl sec-butyl ether. This was considered as evidence for a cleavage recombination mechanism, since the migrating group underwent extensive racemization rather than predominant retention as expected by the carbanion mechanism (which may be considered as an internal nucleophilic substitution). Lansbury and Pattison[25] report support for this mechanism on the basis of isolating products resulting from capture of the intermediate aldehyde by the carbanion portion of the metallating base, the proportion of such product (VII) increasing with the cation-solvating ability of the solvent.



In a similar manner the rearrangement of 2,2,3-triphenylpropyllithium (I) could proceed by elimination of benzyllithium followed by addition of the benzyllithium to the resulting diphenylethylene yielding 1,1,3-triphenylpropyllithium (III). If the rearrangement occurred in this manner



(24) U. Schollkopf and W. Fabian, Ann., 642, 1 (1961).

(25) P. T. Lansbury and V. A. Pattison, Abstracts of American Chemical Society Meeting, Washington, D. C., March 1962, p. 20-O.

the more stable benzyl carbanion would be expected to be eliminated in preference to the less stable phenyl carbanion. Therefore the observed products could be rationalized on the basis of this mechanism also. However, in the related rearrangement of 2-chloro-1,1,1-triphenylethane with sodium, Zimmerman and Smentowski[26] found that running the reaction with added 1,1-di-p-tolyl-2-phenylethylene or triphenylethylene-2-C^{14} led to only minor incorporation of the marked molecules into the product. In the rearrangement of 2-phenyl-2-(p-tolyl)-propyllithium Zimmerman and Zweig[17] excluded this mechanism by demonstrating that p-tolyllithium did not add to 1-methyl-1-phenylethylene under the reaction conditions employed for the rearrangement. The reports do not entirely rule out the elimination addition mechanism for rearrangement of 2,2,3-triphenylpropyllithium since the elimination of a benzyl carbanion should be more facile than the elimination of phenyl or p-tolyl as required in the above examples. If the elimination did occur the readdition would be expected since butyllithium is known[27] to add to triphenylethylene.

Reaction of 1-Chloro-2-methyl-2-phenylpropane (Neophyl Chloride) with Lithium.--The reaction of neophyl chloride with lithium in tetrahydrofuran at -65° for 3-1/2 hours produced a bright yellow solution. Carbonation of this solution produced a 66 per cent yield of carboxylic acid which was shown to be nearly pure 3-methyl-3-phenylbutanoic acid by comparison with an authentic sample. Thus neophyl chloride reacts with

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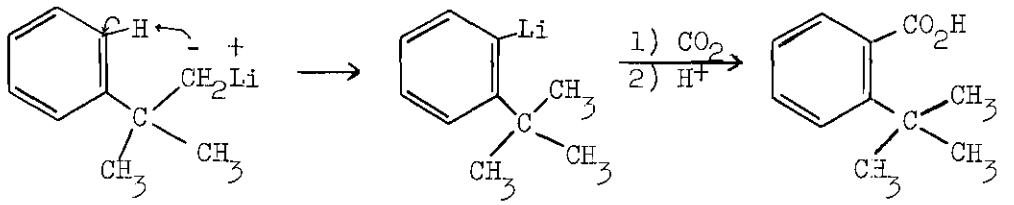
(26) H. E. Zimmerman and F. J. Smentowski, Petroleum Research Fund Report Number Three, American Chemical Society, Washington, D. C., p. 34.

(27) A. G. Evans and D. B. George, J. Chem. Soc., 141 (1962).

lithium at -65° to give 2-methyl-2-phenylpropyllithium which is relatively stable at this temperature. Solutions of 2-methyl-2-phenylpropyllithium prepared as described above were warmed to various temperatures in an effort to obtain a rearrangement of the organolithium compound. Such a solution was warmed to 30° for 4 hours and carbonated. The carbonated solution yielded some 4 per cent of an acidic yellow oil. Most of the neutral material obtained from this reaction was inadvertently lost by volatilization while removing the solvents in vacuo on the steam bath. The above acidic oil was methylated with diazomethane and analyzed by vapor-phase chromatography (details given in experimental chapter). The acidic oil was shown to contain none of the following acids: 3-methyl-3-phenylbutanoic acid; 2-methyl-2-phenylbutanoic acid; 2,2-dimethyl-3-phenylpropanoic acid; ortho-, meta-, and para-t-butylbenzoic acids. The 2-methyl-2-phenylbutanoic acid was expected if a methyl group migrated and 2,2-dimethyl-3-phenylpropanoic acid if a phenyl group migrated. The possible origin of the substituted benzoic acids will be discussed in the details of the next reaction. The vapor-phase chromatography did show the presence of three esters (relative amounts of 32, 29, and 6 per cent based on measurements of peak areas) of volatilities (or retention times) of about the same magnitude as the esters of the six acids mentioned above.

The very small yield of carboxylic acids obtained in the reaction that was warmed to 30° for four hours suggested that very little organolithium compound had survived, so less vigorous conditions were tried. Another solution of 2-methyl-2-phenylpropyllithium was prepared at -65° as before and allowed to warm to 0° and was stirred at that temperature for one hour before carbonation. The carbonated solution gave a 25 per

cent yield of carboxylic acids. Vapor-phase chromatography of these carboxylic acids (as their methyl esters) gave 98 per cent of 3-methyl-3-phenylbutanoic acid and about 2 per cent of ortho-t-butylbenzoic acid most likely results from an intramolecular rearrangement of 2-methyl-2-phenylpropyllithium in which the carbanion group abstracts a proton from the ortho-position of the adjacent phenyl group as shown below:



Zimmerman and Zweig[17] have reported an analogous ortho-substituted benzoic acid which resulted from carbonation of 2,2-diphenylpropyllithium. The neutral material which resulted from the above reaction was also analyzed by vapor-phase chromatography (details in experimental chapter) and found to contain 58 per cent of 2-methyl-2-phenylpropane and 8.4 per cent of 2-phenylbutane and/or 2-methyl-1-phenylpropane; (no conditions could be found which would separate these two compounds). Three more compounds in yields of 5 per cent of each were separated which had somewhat longer retention times (up to 50 per cent longer) but these were not identified. The 2-phenylbutane could arise from the organolithium compound resulting from methyl migration and the 2-methyl-1-phenylpropane from phenyl migration. That the 8.4 per cent of rearranged hydrocarbons did not result from impurities in the neophyl chloride was shown in the following manner. A sample of the neophyl chloride used in these reactions was reacted with sodium in dioxane--t-amyl alcohol. The resulting

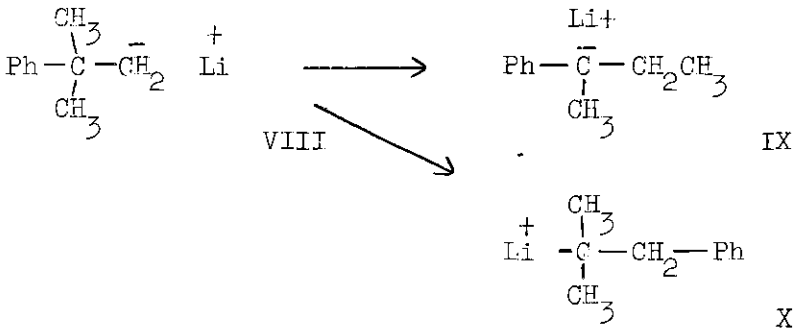
hydrocarbons were analyzed by vapor-phase chromatography and shown to contain 98.3 per cent of 2-methyl-2-phenylpropane. Thus any impurities in the neophyl chloride were far less than the amount of rearranged hydrocarbon found.

In another attempt to effect rearrangement a solution of 2-methyl-2-phenylpropyllithium, prepared at -65°, was warmed to 0°, liquid sodium–potassium alloy added and the mixture was stirred at that temperature for one hour before carbonation. The resulting 16 per cent yield of acids was subjected to vapor-phase chromatography and shown to contain 88 per cent of 3-methyl-3-phenylbutanoic acid, 2 per cent of ortho-t-butylbenzoic acid and small amounts of two unidentified acids with retention times in the range of the six acids analyzed for but identical to none of them. The neutral material isolated from this reaction was analyzed by vapor-phase chromatography and found to contain 30 per cent 2-methyl-2-phenylpropane and 5 per cent 2-phenylbutane and/or 2-methyl-1-phenylpropane.

Thus neophyl chloride has been found to react with lithium in tetrahydrofuran at -65° to give 2-methyl-2-phenylpropyllithium which is fairly stable at that temperature. However, it is only moderately stable at 0° and is completely decomposed in four hours at 30°. No evidence for either of the organolithium compounds which would result from methyl or phenyl migration was found in the acidic products. In the neutral products a small amount of one or both of the hydrocarbons which would result from the rearranged organolithium compounds is found but the major hydrocarbon found results from the unrearranged organolithium compound. Therefore, the 2-methyl-2-phenylpropyllithium apparently is decomposed (protonated by the solvent) much faster than it rearranges. The cleavage of

the ether used as solvent is known to be a serious side reaction in the preparation and reactions of organolithium compounds. Gilman and Gaj[28] report that stability data indicate that the workable temperatures for methyl-, n-butyl- and phenyllithium in tetrahydrofuran are 0°, below -30°, and 0 to 30°, respectively. Gilman and McNinch[29] have found that in the preparation of benzyllithium in tetrahydrofuran temperatures of -5° or below are necessary for good yields of benzyllithium. Hanbein[30] reports that the order of increasing stability of organolithium compounds to boiling diethyl ether is: t-butyl < sec-butyl = iso-propyl = cyclohexyl < iso-butyl < n-propyl < ethyl < n-butyl < n-pentyl < 1-napthyl < phenyl < p-dimethylaminophenyl < p-biphenyl < methyl.

One of the organolithium compounds expected from rearrangement of the 2-methyl-2-phenylpropyllithium would not be expected to be very stable.



The starting organolithium compound (VIII) is a primary carbanion and, as might be expected, is only moderately stable at 0° in tetrahydrofuran. Phenyl migration would lead to X which is a tertiary carbanion with three

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(28) H. Gilman and B. J. Gaj, J. Org. Chem., 22, 1165 (1957).

(29) H. Gilman and H. A. McNinch, ibid., 26, 3723 (1961).

(30) A. H. Hanbein, Iowa State College Journal of Science, 18, 48 (1943).

alkyl substituents and should be very unstable, as is t-butyllithium. Methyl migration would lead to IX which is also a tertiary carbanion but is much more stable since it is a substituted benzyl carbanion. It should have comparable stability to 1-benzyl-1-phenylethyllithium which Zimmerman and Zweig[17] prepared in refluxing diethyl ether. Therefore, if methyl had migrated the resulting organolithium compound should have had sufficient stability to permit isolation as the corresponding acid. The organolithium compound resulting from phenyl migration would not be expected to be stable enough to permit isolation as the corresponding acid but would be rapidly protonated by the solvent. This could account for some or all of the 5-8 per cent yield of 2-phenylbutane and/or 2-methyl-1-phenylpropane found by vapor-phase chromatography.

Steric strain seems to be an important factor in determining whether an organometallic compound will undergo rearrangement. The 2-methyl-2-phenylpropyllithium may have a lack of steric strain since it has only one large substituent on the beta-carbon. Thus far all of the hydrocarbon carbanions which have been found, in this research and by Zimmerman[8,17] and co-workers, to undergo rearrangement have had a quarternary carbon, bearing two or three large substituents, which was converted by rearrangement into a trigonal carbon bearing one less large substituent.

CHAPTER III

EXPERIMENTAL DETAILS

Reactions of 2-Chloro-1,1,1-triphenylethane

Tetrahydrofuran.--Anhydrous tetrahydrofuran was prepared by heating at reflux a commercial grade of tetrahydrofuran containing finely divided molten potassium which was vigorously stirred in a Morton high-speed stirring apparatus[31] for one hour with final distillation of the tetrahydrofuran from the potassium through a Vigreux column, 35 cm. in length. In some of the earlier experiments tetrahydrofuran was purified by distillation from the sodium addition product of anthracene. In the experiments with lithium, tetrahydrofuran purified as above was heated at reflux with lithium aluminum hydride, and then distilled directly into the apparatus for conducting the reaction with lithium metal.

1,2-Dimethyoxyethane.--Eastman Kodak white label grade 1,2-dimethoxyethane was purified over potassium in the same manner as for tetrahydrofuran.

Triethylamine.--Eastman Kodak white label grade triethylamine was purified by treatment of a 500 ml. portion with 30 ml. of benzoyl chloride and removal of the resulting white precipitate by filtration. The remaining liquid was heated at reflux for one hour with 30 ml. of additional benzoyl chloride and after cooling was filtered again. The product was distilled and the distillate allowed to stand for several hours over potassium hydroxide pellets. The resulting clear solution was then treated

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(31) A. A. Morton and L. M. Redman, Ind. Eng. Chem., 40, 1190 (1948).

with potassium in the same manner as described for tetrahydrofuran.

2-Chloro-1,1,1-triphenylethane.--A quantity of this halide, m.p. 101.0 - 101.8°, which had been prepared by Dr. Erling Grovenstein, Jr.[6] was available.

Triphenylsuccinic Anhydride.--A sample of this anhydride, m.p. 113-114°, which had been prepared by Dr. Erling Grovenstein, Jr.[6] was available.

2,2,3-Triphenylpropanoic Acid.--A sample of this acid, m.p. 130.0-131.5°, which had been prepared by Dr. Erling Grovenstein, Jr.[6] by the procedure of Ramart[32] was available.

Diphenylacetic Acid.--Matheson, Coleman, and Bell diphenylacetic acid was purified by vacuum sublimation, m.p. 145-147°.

3,3,3-Triphenylpropanoic Acid.--This acid was prepared by the method of Fosse[33] as elaborated by Hellerman.[34] A mixture of 25.0 g. (0.096 moles) of triphenylcarbinol and 16.5 g. (0.159 moles) of malonic acid was placed in a 250 ml. round bottomed flask fitted with Claisen head, condenser, and receiver. The flask was then heated by means of an oil bath held at 160°. The resulting melt evolved a gas for two hours and was held at 160° for a total of three hours. The melt was then poured into a mortar, allowed to solidify, and ground into a yellow powder. This powder was added to a solution of 10 g. of sodium hydroxide in 400 ml. of water and heated on the steam bath. The aqueous solution was then cooled, extracted with ether, and acidified. The acidification yielded 16.0 g. (55 per cent yield) of

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(32) P. Ramart, Bull. soc. chim. (France), [4] 35, 196 (1924).

(33) R. Fosse, Compt. rend., 145, 197 (1907).

(34) L. Hellerman, J. Am. Chem. Soc., 49, 1735 (1927).

a yellow acid. Decolorizing with charcoal and three recrystallizations from ethanol yielded 10.5 g. of acid of m.p. 178.0-179.5°. Vacuum sublimation of a 0.50 g. portion of this acid at 185° and 45 microns yielded 0.44 g. of m.p. 179.2-180.3°.

Reaction of 2-Chloro-1,1,1-triphenylethane with Potassium.--The apparatus consisted of a 500 ml. Morton flask (two creases, inverted cone) and a Morton high-speed stirrer. To one neck of the flask a 35 cm. Vigreux column was attached to act as an air-cooled condenser and to the other was attached, by large diameter rubber tubing, a flask containing the 2-chloro-1,1,1-triphenylethane (10.0 g., 34.3 mmoles). To the flask was added 200 ml. of purified anhydrous tetrahydrofuran and 4.7 g. (0.12 g. atom) of freshly cut potassium metal. The apparatus was swept with nitrogen and kept under an atmosphere of nitrogen. The solvent was heated to the boiling point, stirring was commenced, and the chloride was dusted into the reaction mixture over a period of 30 minutes and stirring and heating were maintained for another 30 minutes. The first portion of the halide added caused a deep red color to appear in the solution and the final color was like that of bromine. After cooling to room temperature, the contents of the flask were forced onto a large excess of crushed solid carbon dioxide. The next day 50 ml. of absolute ethanol was added to decompose any unreacted potassium. The following day the reaction mixture was made slightly acidic by addition of gaseous hydrogen chloride and the solvents were removed on the steam bath under partial vacuum. The residue was treated with an excess of aqueous sodium hydroxide and 3.4 g. of neutral material was extracted with ether. Acidification and extraction with ether gave, in the ether extract, 4.91 g. of crude acids, m.p. 99-134°.

A 3.62 g. sample of the crude acids in chloroform was subjected to chromatography on a column, 3.4 cm. in diameter, packed to a height of 14 cm. with silicic acid (Mallinckrodt, 100 mesh, analytical reagent grade) wetted with chloroform. The column was eluted with chloroform containing increasing amounts of methanol.* The first acid eluted from the column weighted 3.25 g. and had m.p. 100-120°. One recrystallization of 3.0 g. of this acid from ethyl alcohol gave 1.7 g. of acid, m.p. 129-131°. This acid was found to be identical with authentic 2,2,3-triphenylpropanoic acid (m.p. 130.0-131.5°) as shown by mixed melting point and infrared spectral determinations. The second acid eluted from the column weighed 0.33 g. and had m.p. 129-140°. A 0.193 g. sample of this acid upon recrystallization from ethyl alcohol gave 0.136 g. of acid, m.p. 140-142°. A second recrystallization from ethyl alcohol gave 0.100 g., m.p. 143-145°. A 0.0966 g. sample of this acid was titrated with 0.01297 Normal sodium hydroxide solution to the phenolphthalein end point and a neutral equivalent of 219 was obtained. This neutral equivalent is close to the theoretical value of 212 for diphenylacetic acid and much smaller than the value of 302 for a triphenylpropanoic acid. A sample of this acid obtained in the following run by the same procedure was sublimed at 50 microns and a bath temperature of about 115°. This sublimed acid was recrystallized from cyclohexane and had m.p. 145-146°. This acid was found to be identical** with authentic diphenylacetic acid, m.p. 145-147°, as

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*The author is indebted to Dr. John Dyer for instruction in the technique of this chromatography.

**The author is indebted to Dr. Jack Hine for first suggesting diphenylacetic acid for the possible identity of this acid.

shown by mixed melting point and infrared spectral determinations.

A second reaction between 2-chloro-1,1,1-triphenylethane and potassium metal was carried out exactly as in the first run except that the tetrahydrofuran and potassium were heated under reflux with vigorous stirring for 30 minutes before addition of the alkyl chloride. This apparently resulted in a much drier reaction medium as evidenced by a considerable increase in the yield of acids. The yield of acids was 7.79 g. and this material upon chromatography gave 6.7 g. of crude 2,2,3-triphenylpropanoic acid and 0.31 g. of crude diphenylacetic acid, with most of the remainder of the product being an intermediate fraction.

Liquid sodium-potassium alloy was prepared in the usual apparatus from 4.7 g. of potassium and 0.53 g. of sodium in 200 ml. of tetrahydrofuran heated at reflux with stirring. The mixture was cooled to room temperature and 11.0 g. of 2-chloro-1,1,1-triphenylethane was added over a period of 25 minutes with stirring continued for an additional 30 minutes while the temperature was maintained at 20 ± 3° with a cooling bath. The mixture was carbonated and worked up in the usual manner to give 6.22 g. of acids and 3.6 g. of neutral product. Chromatography on silicic acid showed that the product was predominately 2,2,3-triphenylpropanoic acid with about 0.1 g. of diphenylacetic acid.

Liquid sodium-potassium alloy prepared as above from 6.4 g. of potassium and 1.6 g. of sodium was treated in 250 ml. of tetrahydrofuran at ± 3° with 10.0 g. of 2-chloro-1,1,1-triphenylethane by slow addition of the latter over a period of 30 minutes. The mixture was then stirred for an additional hour at this temperature and then carbonated. The first addition of the halide to the alloy caused the development of the red

color which rapidly deepened as usual to the color of liquid bromine. The usual work up of the reaction mixture yielded 3.36 g. of acid whose infrared spectrum indicated that it was essentially all 2,2,3-triphenylpropanoic acid. The neutral material from this run gave a strong positive test for chloride upon sodium fusion; therefore, evidently considerable unreacted starting material was recovered.

In the usual apparatus 4.72 g. of potassium metal in 250 ml. of 1,2-dimethoxyethane was heated at reflux with stirring for 10 minutes and then, with stirring stopped, the mixture was cooled to the freezing point of the solvent (-58°). After stirring for 30 minutes at this temperature the solution acquired a pale blue color which rapidly developed into a deep blue-black color. This color was observed to persist in the temperature range of -58 to 35°. With the reaction mixture maintained at -50 ±5°, a small portion of 2-chloro-1,1,1-triphenylethane was added. An immediate red-brown color was produced and after stirring about 10 minutes more the blue-black color reappeared. After approximately one gram of the alkyl halide had been added in this manner, the potassium sand suddenly agglomerated and stirring had to be stopped to prevent breaking the reaction vessel. The mixture was then carbonated and yielded 0.70 g. of acids and 0.34 g. of neutral material. The acidic fraction was sublimed twice at 50 microns and at a bath temperature of about 200° to give 0.34 g. of pale yellow crystals, m.p. 68-110°. The infrared spectrum of this material showed that it contained triphenylsuccinic anhydride and 2,2,3-triphenylpropanoic acid. This mixture was treated with hydrazine (details given in the following section on reactions of 2-chloro-1,1,1-triphenylethane with lithium) to give 0.12 g. of crude cyclic triphenylsuccinic hydrazide

and 0.26 g. of acidic material. The acidic fraction upon silicic acid chromatography gave 0.11 g. of essentially pure 2,2,3-triphenylpropanoic acid with the remainder of the acidic fraction also being chiefly this acid according to its infrared absorption spectrum.

Reaction of 2-Chloro-1,1,1-triphenylethane with Lithium.--The apparatus and general procedure for conducting the reactions with lithium was the same as that for the potassium experiments except that the 2-chloro-1,1,1-triphenylethane (10.0 g., 34.3 mmoles) was dissolved in 25 ml. of tetrahydrofuran and added from a dropping funnel through a side-arm of the reaction flask. In 250 ml. of freshly distilled tetrahydrofuran was placed 0.62 g. (0.0883 g. atom) of lithium ribbon chopped into small pieces. The lithium ribbon was a low-sodium grade (0.005 per cent Na max.) obtained from the Lithium Corp. of America. A small portion of the halide solution was added to the reaction mixture at -30°, but when after 40 minutes at this temperature no reaction was apparent, the temperature was raised to -10° and a red color was observed in 10 minutes. As soon as the red color was noticed, indicating reaction, the reaction mixture was again lowered to -30 ±5° and the rest of the halide solution was added dropwise over a period of 30 minutes. The reaction mixture was stirred at -30° for another 30 minutes and then carbonated. The final color of the solution, before carbonation, was a purple-black, very similar to that of potassium permanganate solutions. During the carbonation step approximately half of the reaction mixture was lost because of excessive frothing. About 25 ml. of water was added to decompose any unreacted lithium and the reaction mixture was worked up in the same manner as the potassium experiments. The yield was 2.35 g. of neutral material and 2.82 g. of

acidic material, m.p. 165-174°. A 1.9 g. sample of the acidic material upon chromatography on silicic acid gave 1.8 g. of acid of m.p. 165-179°; this acid upon recrystallization from ethyl alcohol gave 1.1 g. of acid, m.p. 179-180°. This acid was shown to be identical with authentic 3,3,3-triphenylpropanoic acid, m.p. 179.2-180.3°, by a mixed melting point determination and by intercomparison of infrared spectra. The remaining 0.1 g. of acid from the chromatography, which was the initial acid to come off the column, was noncrystalline; its infrared spectrum indicated that it was a mixture of 3,3,3-triphenylpropanoic acid and 2,2,3-triphenylpropanoic acid.

The next reaction of 2-chloro-1,1,1-triphenylethane with lithium at 28 ±3° was carried out on the same scale and by the same technique as for the first reaction. An attempt to initiate this reaction at 66° was unsuccessful as judged by the lack of the appearance of the usual red color. At -10° two hours of vigorous stirring were required to initiate the formation of the red color which indicated reaction. The halide was then added dropwise at -10° over a period of 30 minutes. The solution was allowed to warm to 28° and was stirred at this temperature for one hour and then carbonated. The usual work-up yielded 5.30 g. of neutral material and 3.49 g. of acidic material. The ultraviolet absorption of the neutral material at 300 millimicrons indicated the presence of about 8 per cent by weight of triphenylethylene. The molecular extinction (ϵ) of triphenylethylene at 300 millimicrons is 20,000.[6] Chromatography of a 2.7 g. sample of the acids on silicic acid gave as a first fraction 0.86 g. of compound, m.p. 109-113°, which was identified as triphenylsuccinic anhydride (m.p. 113-114°) by comparison of its infrared spectrum with that

of an authentic sample. A second fraction of 1.28 g., m.p. 119-129°, was essentially 2,2,3-triphenylpropanoic acid according to comparison of its infrared spectrum with that of an authentic sample. Recrystallization of a 0.12 g. sample of the second fraction from ethyl alcohol gave 0.066 g. of acid, m.p. 130.5-131°, as expected for pure 2,2,3-triphenylpropanoic acid. A third fraction of 0.45 g. was a glassy material of which only 40 per cent could be distilled at 20 microns and a bath temperature up to 190°; the infrared spectrum of the distillate was identical with the spectrum of 2,2,3-triphenylpropanoic acid.

In an attempt to analyze more accurately the acid mixtures in these reactions, the following method of infrared spectral analysis was developed. All infrared spectra were determined with a Perkin-Elmer double beam Model 21 infrared spectrometer. Triphenylsuccinic anhydride has a characteristic absorption maxima at 5.581 microns. 2,2,3-Triphenylpropanoic acid has absorption maxima at 7.900 microns and 13.856 microns which distinguish it from 3,3,3-triphenylpropanoic acid which has characteristic absorption maxima at 8.138 microns and 13.225 microns. Diphenylacetic acid, which may be present in small amount in these acid mixtures, has characteristic absorption maxima at 9.000 and 13.700 microns. Diphenylacetic acid has moderate absorption at 13.856 microns and very weak absorption at 5.581, 7.900, 8.138, and 13.225 microns; therefore, a small amount of this acid should not affect the accuracy of this method very much. For the quantitative analysis solutions containing 0.0480 g. of acid in 10.0 ml. of carbon disulfide were placed in 3 mm. rock salt cells and measured at the five wave lengths, except for pure triphenylsuccinic anhydride which was measured at 5.581 microns using a solution containing 0.0060 g. of triphenyl-

succinic anhydride in 10 ml. of carbon disulfide. The more dilute anhydride solution was necessary because its absorption at 5.581 microns was much greater than the absorption at the other four wave lengths. A series of calibration curves were prepared using known mixtures of 2,2,3-triphenylpropanoic acid and 3,3,3-triphenylpropanoic acid. Mixtures containing 0, 25, 50, 75, and 100 per cent of one acid and the remainder of the other acid were used. Solutions containing 0.0480 g. of the mixture in 10 ml. of carbon disulfide were measured at 7.900, 8.138, 13.225, and 13.856 microns and the optical density readings obtained were plotted against percentage to give a series of curves (Figure 1). Using this method, mixtures could be analyzed with an accuracy of about two per cent when only a few per cent of triphenylsuccinic anhydride was present. When larger percentages of the anhydride were present in the mixtures, better results were obtained by the following mathematical treatment of the data. The following extinction coefficients for both acids and the anhydride were determined at each of the five wave lengths.

Table 1. Extinction Coefficients of Triphenylsuccinic Anhydride, 2,2,3-Triphenylpropanoic Acid, and 3,3,3-Triphenylpropanoic Acid

Wave Length, microns	Extinction Coefficients		
	Triphenylsuccinic Anhydride	2,2,3-Triphenyl-propanoic Acid	3,3,3-Triphenyl-propanoic Acid
5.581	980.0	23.3	29.0
7.900	46.5	122.0	49.4
8.138	135.0	62.7	179.0
13.225	127.0	34.6	97.5
13.856	63.7	141.0	54.0

Using these extinction coefficients (E), the optical density (D) of the mixture at each of the five wave lengths, and the following series of equations one may solve for the amount of triphenylsuccinic anhydride (C_1), 2,2,3-triphenylpropanoic acid (C_2), and 3,3,3-triphenylpropanoic acid (C_3) in the mixture. At one wave length the optical density of the mixture is determined by the following equation:

$$D = C_1E_1 + C_2E_2 + C_3E_3$$

Substituting the extinction coefficients at each wave length gives:

$$D_1 = 980.0\ C_1 + 23.3\ C_2 + 29.0\ C_3$$
$$D_2 = 46.5\ C_1 + 122.0\ C_2 + 49.4\ C_3$$
$$D_3 = 135.0\ C_1 + 67.7\ C_2 + 179.0\ C_3$$
$$D_4 = 127.0\ C_1 + 34.6\ C_2 + 97.5\ C_3$$
$$D_5 = 63.7\ C_1 + 141.0\ C_2 + 54.0\ C_3$$
$$.00480 \text{ g./ml.} = C_1 + C_2 + C_3$$

Substituting the optical density measured at each of the five wave lengths into the above equations and knowing that .00480 g./ml. is the total concentration of acids in the solutions analyzed gives six simultaneous equations with three unknowns. Adding three pairs of the equations gives three simultaneous equations with three unknowns which were solved by the usual method. This method proved to be the best method for analyzing mixtures of these acids.

Another reaction of 2-chloro-1,1,1-triphenylethane with lithium was carried out on the same scale in the usual manner. Reaction was initiated in 80 minutes after addition of a small amount of halide at -10°. The reaction mixture was then cooled to -55 ±5° and the remainder of the

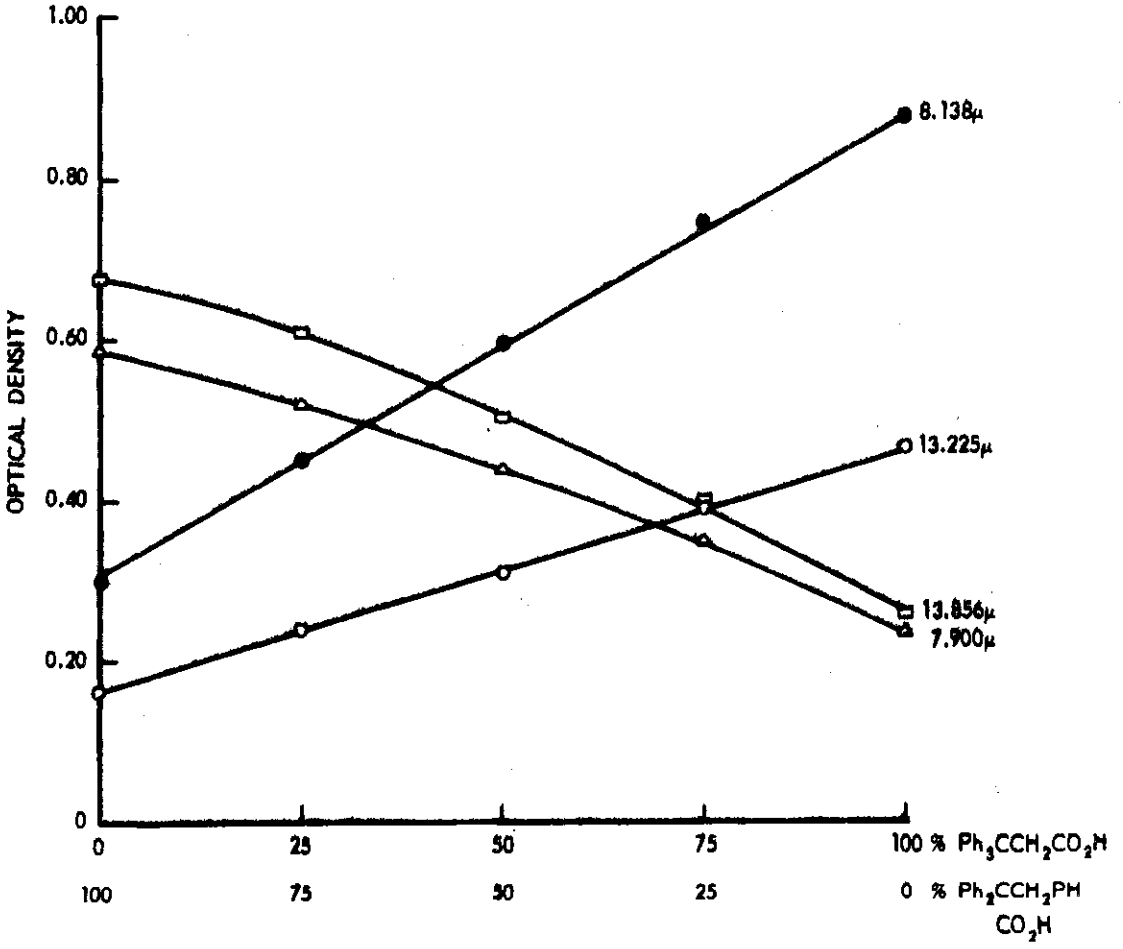

Figure 1. Calibration Curves for Infrared Analyses of Binary Mixtures of 2,2,3-Triphenylpropanoic Acid and 3,3,3-Triphenylpropanoic Acid.

halide solution was added over a period of 30 minutes with stirring for an additional 30 minutes at -55° before carbonation. The usual work-up yielded 4.88 g. of neutral material and 4.46 g. of acidic material. The acidic material had m.p. 173-179°, which is close to that of pure 3,3,3-triphenylpropanoic acid (m.p. 179-180°). Infrared spectra on a sample sublimed at 20 microns and a bath temperature of 200° confirmed that the crude acid was predominantly 3,3,3-triphenylpropanoic acid and showed the presence of a trace (about 3 per cent) of 2,2,3-triphenylpropanoic acid and about 0.7 per cent of triphenylsuccinic anhydride. Presumably the 2,2,3-triphenylpropanoic acid resulted from 1,1,2-triphenylethyl carbanion which was formed during initiation at -10° and must have been responsible for the deep red-purple color of the solution. A sodium fusion test on the neutral material gave a strong test for chloride ion and following reactions at low temperatures were run for longer times.

Another reaction on the same scale between the halide and lithium was initiated after stirring for 3.5 hours at -10°. The major portion (at least 96 per cent) of the halide was added at -60 ±5° over a period of 30 minutes and the reaction mixture was stirred at this temperature for three hours before carbonation. The usual work-up yielded 3.43 g. of neutral material and 6.42 g. of acid, m.p. 174-176°. Infrared spectral analysis of a sample of this acid which had been sublimed at 20 microns and a bath temperature of 180° showed that the acid was 94 per cent pure 3,3,3-triphenylpropanoic acid containing about 3 per cent of 2,2,3-triphenylpropanoic acid and about 3 per cent of triphenylsuccinic anhydride. The neutral material was subjected to a sodium fusion test and gave only a weak test for chloride ion.

Another run was made exactly like the previous one except that after stirring for three hours at -60° it was allowed to warm to 0° and was maintained at this temperature with stirring for one hour before carbonation. The usual workup yielded 4.21 g. of neutral material and 5.35 g. of acidic material. Chromatographic separation of the acidic material on a column of silicic acid was not very successful, partly because triphenylsuccinic anhydride tended to come off the column both in the form of the free acid and as the anhydride. The following method of separation was based on the reaction of the anhydride with hydrazine.

Triphenylsuccinic anhydride (0.50 g.) and 5.0 ml. of hydrazine hydrate were placed in a flask fitted with a condenser and the mixture was heated on the steam bath for one hour. The mixture was cooled to room temperature and the crystals which precipitated were removed by filtration and washed with water. After drying in vacuo at 78°, the crystals had m.p. 180-181.5° and weighed 0.50 g. (96 per cent yield). The product was sublimed at a bath temperature of 190-196° and a pressure of 15 microns without change in melting point and gave the following analysis.*

Anal. Found: C, 77.46; H, 5.42; N, 7.94. Calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18.

This compound, therefore, appears to be a cyclic hydrazide of triphenylsuccinic acid. 3,3,3-Triphenylpropanoic acid (0.50 g.) was treated with 5.0 ml. of hydrazine hydrate under the conditions given above. After cooling to room temperature 150 ml. of water was added to

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*Analysis by Galbraith Microanalytical Laboratories.

the reaction mixture and it was made acidic with hydrochloric acid. The precipitated acid was separated by filtration, washed with water and dried in vacuo. The yield of recovered 3,3,3-triphenylpropanoic acid, m.p. 178-180°, was 0.47 g. (94 per cent).

2,2,3-Triphenylpropanoic acid (0.50 g.) was treated with hydrazine hydrate under the conditions given above. The above work-up yielded 0.45 g. of impure 2,2,3-triphenylpropanoic acid, m.p. 95-115°. This acid was purified by redissolving it in aqueous hydrazine solution and extracting with three portions of chloroform. The usual work-up of the aqueous hydrazine solution and vacuum sublimation of the resulting acid gave 0.35 g. (70 per cent) of pure 2,2,3-triphenylpropanoic acid.

The acids from the last run above were sublimed at 20 microns and a bath temperature up to 189° with about 90 per cent recovery of acids and removal of a small amount of tarry material (previous experiments had shown that both of the triphenylpropanoic acid and the anhydride could be sublimed under these conditions with 90 per cent or better recovery of acids of unchanged m.p. and that most of the loss was due to mechanical transfer). A 1.00 g. sample of the sublimed acids after heating for one hour on the steam bath with 5.0 ml. of hydrazine hydrate and steam distillation of most of the excess hydrazine gave 0.35 g. of crude hydrazide upon extraction of the aqueous solution with chloroform. Acidification and extraction with ether gave 9.69 g. of acids. Sublimation at 20 microns and 180° gave 0.59 g. of acids. Sublimation at 20 microns and 180° gave 0.59 g. of acids. Analysis of these acids by infrared absorption by the technique previously described gave 38 ±8 per cent 3,3,3-triphenylpropanoic acid, 62 ± 8 per cent of 2,2,3-triphenylpropanoic acid and

about 0.5 per cent of triphenylsuccinic anhydride.

Another reaction on the same scale of 2-chloro-1,1,1-triphenylethane with lithium at -60° for 3.5 hours and then at 0° for one hour and carbonation was carried out. The usual work-up yielded 5.17 g. of neutral material and 3.57 g. of acidic material. This acid material was reacted with hydrazine as previously described except that 95% hydrazine was used instead of hydrazine hydrate (64 per cent hydrazine). This gave 1.75 g. of crude hydrazide and 1.36 g. of acids. These acids were sublimed and separated by chromatography on silicic acid. The chromatography showed 30 per cent 3,3,3-triphenylpropanoic acid, 60 per cent 2,2,3-triphenylpropanoic acid and the remainder a mixture of these two acids. Since the amount of crude hydrazide in this reaction seemed unusually large (1.75 g.), it was subjected to vacuum sublimation at 25 microns and 200° and only .56 g. of hydrazide sublimed. The non-sublimable material was heated on the steam bath for two hours in 50 ml. of a ten per cent solution of sodium hydroxide in ethyl alcohol. Cooling, extraction with ether, acidification and extraction with ether yielded 0.58 g. of acidic material of which 0.27 g. could be sublimed under the usual conditions. This 0.27 g. of acids was analyzed by the infrared absorption technique and found to contain 30 per cent triphenylsuccinic anhydride, 23 per cent 3,3,3-triphenylpropanoic acid and 47 per cent 2,2,3-triphenylpropanoic acid. Apparently the 95 per cent hydrazine used in this reaction is somewhat more reactive toward the two triphenylpropanoic acids than is hydrazine hydrate and led to some other neutral impurities as well.

A reaction of 2-chloro-1,1,1-triphenylethane with lithium at -60° for three hours and then at 0° with sodium-potassium alloy added (6.4 g.

of K and 1.6 g. of Na) for one hour and then carbonation was carried out. This reaction yielded 3.84 g. of neutral material and 5.91 g. of acidic material. Treatment of the acidic material with 95 per cent hydrazine as described above yielded 2.76 g. of crude hydrazide and 2.64 g. of acids. These acids were sublimed and separated by chromatography on silicic acid. The chromatography showed 23 per cent 3,3,3-triphenylpropanoic acid, 73 per cent 2,2,3-triphenylpropanoic acid and the remainder a mixture of these two acids. The 2.76 g. of crude hydrazide was sublimed at 25 microns and 200° and 1.52 g. of hydrazide sublimed. The remaining material was treated with sodium hydroxide as described in the previous experiment and yielded 0.38 g. of acidic material. This was sublimed to give 0.33 g. of acids which were analyzed by the infrared absorption technique and found to contain 14.2 per cent triphenylsuccinic anhydride, 30 per cent 3,3,3-triphenylpropanoic acid and 56 per cent 2,2,3-triphenylpropanoic acid.

A reaction to test the effect of added triethylamine was made with the usual quantities of reactants in 200 ml. of tetrahydrofuran. Reaction between 2-chloro-1,1,1-triphenylethane and lithium on the usual scale was initiated after stirring 40 minutes at -10° and the remainder of the halide solution was added over a period of 30 minutes at a temperature of -65 ±5°. The reaction mixture was stirred for two hours at this temperature and then 100 ml. of cold triethylamine was added with the low temperature being maintained. There was an immediate color change of the reaction mixture from dark red to light orange. The reaction mixture was stirred at -65° for one hour and then carbonated. At the end of the period

of stirring the color of the reaction mixture was again dark red. This reaction yielded 4.10 g. of neutral material and 3.10 g. of acidic material which melted at 175.5-178.0°. The infrared spectrum confirmed that this was essentially pure 3,3,3-triphenylpropanoic acid.

Three attempts were made to effect reaction on the usual scale between 2-chloro-1,1,1-triphenylethane and lithium at -50° in 1,2-dimethoxyethane and all three were unsuccessful. These reactions were initiated in the usual manner at -10° and the usual red color was observed. The reactions were then cooled to -50° and stirred at this temperature for one to three hours in an atmosphere of helium or the usual atmosphere of nitrogen. After carbonation and the usual work-up, these reactions yielded 0.10 to 0.20 g. of acidic material and 8.70 to 9.19 g. of neutral material. The acidic material was shown by infrared spectra to be predominantly triphenylsuccinic anhydride and 2,2,3-triphenylpropanoic acid in nearly equal amounts. The neutral material was shown to be nearly pure starting chloride by its melting point and infrared spectrum.

A reaction on the usual scale between 2-chloro-1,1,1-triphenylethane and lithium metal in 1,2-dimethoxyethane was initiated at -10° and the temperature lowered to -50°. The remainder of the halide was added at -50° and the reaction was stirred at this temperature for three hours. It was then warmed to 0° and stirred at this temperature for one hour and carbonated. The usual work-up yielded 6.78 g. of neutral material and 1.80 g. of acidic material. Two sublimations of the acidic material at 190° and 30 to 50 microns gave 1.11 g. of product, m.p. 95-105°. Recrystallization from ethanol gave 0.81 g. of crystals, m.p. 105-108°, whose infrared spectrum showed the substance to be almost entirely triphenylsuccinic anhydride.

Reactions of 1-Chloro-2,2,3-triphenylpropane

1-Chloro-2,2,3-triphenylpropane.--This chloride* was prepared by the procedure of Dr. E. Grovenstein, Jr.[35] A solution of 1,1,2-triphenylethylpotassium was prepared from 7.5 g. (0.192 g. atom) of potassium and 24 g. (0.082 mole) of 2-chloro-1,1,1-triphenylethane in 500 ml. of tetrahydrofuran by the procedure previously described. The solution was forced under nitrogen through a tube containing a glass-wool plug (to remove particles of unreacted potassium) into a one liter round-bottomed flask and stored under nitrogen overnight. The solution was then forced by nitrogen through a tube into 250 ml. of methylene chloride (which had been freshly distilled and stored over anhydrous calcium sulfate) contained in a one liter Morton flask equipped with a Morton stirrer. The addition of the 1,1,2-triphenylethylpotassium to the methylene chloride was made over a 15 minute period with vigorous stirring at a temperature which was maintained at 15 ±5°. The solution was filtered through a sintered-glass filter and was concentrated on the steam bath, finally in vacuo, to give a brown semi-crystalline mass. This was washed with 15 ml. of acetone giving 16.5 g. of light tan crystals. Recrystallization from acetone gave 12.2 g. of nearly white crystals, m.p. 122-126°. Another recrystallization from acetone gave 10.50 g., m.p. 126-127°. Recrystallization from acetone (with added Nuchar C to decolorize) gave 8.47 g. of white crystals, m.p. 128-129°. Concentration of the combined acetone solutions

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*The author is indebted to Dr. E. Grovenstein, Jr. for supplying much of the 1-chloro-2,2,3-triphenylpropane used in these experiments.

(35) E. Grovenstein, Jr. and L. P. Williams, Jr., J. Am. Chem. Soc., 83, 2539 (1961).

gave brown crystals. These were recrystallized twice from acetone (with added Nuchar C) and gave 1.40 g., m.p. 128-129° or a total of 9.87 g. (38 per cent yield).

Anal. Found: C, 81.78, 82.18; H, 6.39, 6.28; Cl, 11.20, 11.34. Calcd. for $C_{21}H_{19}Cl$: C, 82.20; H, 6.24; Cl, 11.56.

It has been shown[35] that the halide obtained by this synthesis may be reduced to 1,2,3-triphenylpropane by sodium in dioxane--t-amyl alcohol and that the 1,2,2-triphenylpropane from this reaction was identical with a sample prepared from 1,1,2-triphenylethylpotassium and methyl iodide.

3,3,4-Triphenylbutanol-1.--To a solution of 1,1,2-triphenylethylpotassium, prepared from 10.0 g. of 2-chloro-1,1,1-triphenylethane and 4.0 g. of potassium in 250 ml. of tetrahydrofuran, was added 3.0 g. of ethylene oxide dissolved in 25 ml. of tetrahydrofuran. The addition was made at room temperature over a period of 30 minutes with stirring at room temperature contained for an additional 30 minutes. The unreacted potassium was decomposed by slow addition of t-butyl alcohol and then t-butyl alcohol to which water was added. The reaction mixture was neutralized with hydrochloric acid and evaporated on the steam bath in vacuo to dryness. The residue after addition of water was extracted with ether and the ether extract gave 9.8 g. of amorphous product. Some 4 g. of this product was distilled at 0.05 mm. and a bath temperature of 190° to give a pale yellow glass which after two recrystallizations from n-hexane gave 1.16 g. of white crystals, m.p. 105-108°. This product was redistilled in vacuo as before to give 1.01 g. of crystals, m.p. 107.2-108.2°. For analysis this compound was distilled, recrystallized from n-hexane, and redistilled to give 3,3,4-triphenylbutanol-1, m.p. 107.2-108.5°.

Anal. Found: C, 87.17; H, 7.05. Calcd. for $C_{22}H_{22}O$: C, 87.37; H, 7.34.

The remainder of the crude product was chromatographed on silicic acid with chloroform used as solvent and for elution. The main fractions (3.3 g.) after recrystallization from n-hexane and distillation in vacuo gave 2.35 g. of 3,3,4-triphenylbutanol-1, m.p. 104-107°.

3,3,4-Triphenylbutanoic Acid.--One gram of 3,3,4-triphenylbutanol-1, m.p. 104-107°, was dissolved in 22 ml. of benzene and the solution was added slowly with stirring to a solution of 1.26 g. of $Na_2Cr_2O_7 \cdot 2H_2O$ in 7.05 ml. of water, 1.0 ml. of acetic acid and 2.0 ml. of sulfuric acid.* During this addition the reaction mixture was cooled in an ice bath; after completion of the addition the reaction mixture was allowed to warm to room temperature and was stirred for five hours. The benzene layer was separated, washed twice with water, and extracted with five 20 ml. portions of 5 per cent sodium hydroxide solution. The sodium hydroxide extracts and a solid which appeared during the extraction were combined and acidified with sulfuric acid. Extraction of the acidified solution with ether gave 0.74 g. of acidic material, m.p. 145-165°. From the benzene layer 0.36 g. of neutral material was recovered. The acidic material was sublimed (or distilled) twice at 40 microns at a bath temperature of 190°. The sublimate amounted to 0.32 g. of acid, m.p. 160-170°, and a considerable amount of non-distillable black residue remained. The acid after two recrystallizations from benzene yielded 0.18 g. of white crystals, m.p. 171-174°. Another sublimation gave 0.15 g. of acid, m.p. 173-175°.

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*The author is indebted to Dr. John W. Huffman for suggesting this procedure for oxidation.

An attempt to prepare 3,3,4-triphenylbutanoic acid by Arndt-Eistert synthesis from 2,2,3-triphenylpropanoic acid was unsuccessful apparently because of steric hindrance in the reaction of the corresponding acid chloride with diazomethane.[36]

2,2,4-Triphenylbutanoic Acid.--The authentic sample of 2,2,4-triphenylbutanoic acid was prepared from 1,1,3-triphenylpropanol-1 which was made from 2-phenylethylmagnesium bromide and benzophenone after the method of Kharasch and Burt.[37] In the usual apparatus for alkali-metal reactions was placed 19.8 g. (0.81 g. atom) of magnesium turnings and 500 ml. of dry ether. Over a period of 75 minutes 100 g. (0.54 mole) of 2-phenylethylbromide was slowly added with stirring. After addition of the bromide was completed, the reaction mixture was stirred at reflux for 20 minutes. Next 99 g. (0.54 mole) of benzophenone in 200 ml. of ether was added over a period of 45 minutes and stirring at reflux was continued for an additional 30 minutes. After hydrolysis with a saturated solution of ammonium chloride, the combined ether extracts yielded 102 g. of a brown partially crystalline material. Two recrystallizations from ethyl alcohol yielded 33 g. of 1,1,3-triphenylpropanol-1, m.p. 86-88° (reported m.p. 86-88°).

The 1,1,3-triphenylpropanol-1 was converted to its methyl ether by the procedure of Ziegler and co-workers.[38] 1,1,3-Triphenylpropanol-1 (28 g.) was dissolved in 100 ml. of anhydrous methanol and 1.2 ml. of concen-

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(36) W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 45.

(37) M. S. Kharasch and J. G. Burt, J. Org. Chem., 16, 150 (1951).

(38) K. Ziegler, K. Richter and B. Schnell, Ann., 443, 177 (1925).

trated sulfuric acid was added to this solution. The ether rapidly precipitated out and after standing two hours at room temperature the crude ether was obtained by filtration. One recrystallization from acetone yielded 21.9 g. (75 per cent yield) of 1-methoxy-1,1,3-triphenylpropane, m.p. 109-111° (reported m.p. 111-112°).

The 1-methoxy-1,1,3-triphenylpropane was cleaved by NaK alloy by the procedure of Ziegler and co-workers[39] except that instead of shaking with the alloy, stirring with the Morton stirrer was employed. In the usual apparatus for alkali-metal reactions was placed 21 g. (actually less due to accidental spillage) of 1-methoxy-1,1,3-triphenylpropane, 250 ml. of diethyl ether, and 9.0 g. of Na-K alloy (8.0 g. of potassium and 1.0 g. of sodium). The reaction mixture was stirred at room temperature for six hours. At this time 500 ml. of ether was added (some of the original diethyl ether had been swept out by the nitrogen atmosphere) and about half of the reaction mixture was forced onto pulverized solid carbon dioxide. The remainder of the reaction mixture was reacted with 250 ml. of t-butyl alcohol. The carbonated material was treated with aqueous sodium hydroxide, extracted with ether, acidified and extracted again with ether. The ether extract of the acidified solution yielded 3.19 g. of acidic material. This material was recrystallized from benzene twice and sublimed twice at 30 microns and a bath temperature of 200° to yield 1.14 g. of 2,2,4-triphenylbutanoic acid, m.p. 186.1-186.9° (reported m.p. 181°). The part of the reaction mixture that was treated with t-butyl alcohol was heated on the steam bath and the solvents were

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(39) K. Ziegler, F. Crossmann, H. Kleiner and O. Schafer, ibid., 473, 27 (1929).

removed *in vacuo* at that temperature. The resulting 6.43 g. of viscous material was distilled at 30 microns and a bath temperature of 155° to give 5.86 g. of pale yellow crystals. This material was recrystallized from n-pentane and yielded 5.51 g. of 1,1,3-triphenylpropane, m.p. 44-45° (reported[40] m.p. 46°).

Reaction of 1-Chloro-2,2,3-triphenylpropane with Lithium at -65°.--Purified tetrahydrofuran (250 ml.) was distilled from lithium aluminum hydride into the usual apparatus for alkali-metal reactions. To this solvent was added 0.70 g. (0.0997 g. atom) of lithium ribbon which had been cut into small pieces. The protective paraffin coating on the lithium ribbon was removed with dry benzene and the excess benzene removed by blotting the ribbon with a paper towel. The lithium ribbon was of a low-sodium grade (0.005 per cent Na max.) obtained from the Lithium Corp. of America. A small portion of a solution of 8.0 g. (26.1 mmoles) of 1-chloro-2,2,3-triphenylpropane in 25 ml. of tetrahydrofuran was added. When after five hours of vigorous stirring at -10° no evidence of reaction was obtained, 0.6 ml. of methyl iodide was added and a red color was obtained in about 20 minutes. The reaction temperature was lowered to -65 ±5° and the remainder (at least 95 per cent) of the 1-chloro-2,2,3-triphenylpropane was added over a period of 20 minutes. Stirring was continued for three more hours at -65° and then the reaction mixture was forced onto pulverized solid carbon dioxide. The next day the reaction mixture was acidified with 10 per cent hydrochloric acid, which reacted with the remainder of the lithium, and the solvents were removed *in vacuo* at steam-bath temperature. The residue was treated with an excess of aqueous sodium

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(40) H. Wieland and H. Kloss, *ibid.*, *470*, 216 (1929).

hydroxide and 4.18 g. of neutral material was extracted with ether. Acidification and extraction with ether gave, in the ether extract, 3.36 g. of acidic material, m.p. 157-165°. The acidic material was sublimed at 0.05 mm. at a bath temperature of 180-190° to give 2.63 g. (31 per cent yield) of acid, m.p. 170-174°. A 100 g. sample of this acid after two recrystallizations from benzene gave 0.73 g. of acid, m.p. 174.5-175.1°. This acid was identical with a sample of 3,3,4-triphenylbutanoic acid (synthesized by the procedure given previously) according to mixed melting point and infrared spectral comparisons.

Anal. Found: C, 83.86; H, 6.14. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37.

The neutral material from this run was distilled at 0.03 mm. at a bath temperature of 175° to give 3.0 g. of material, m.p. 80-110°. A 1.0 g. sample of this material was recrystallized twice from ethanol to give 0.44 g. of material, m.p. 104-116°. The infrared spectrum of this product indicated that it was 1,2,2-triphenylpropane containing a small amount of 1-chloro-2,2,3-triphenylpropane.

Reaction of 1-Chloro-2,2,3-triphenylpropane with Lithium at -65° and then at 0°.--1-Chloro-2,2,3-triphenylpropane was treated with lithium at -65° in exactly the same manner and with the same quantities of reactants as specified previously for the reaction at -65°. After the three hour stirring period at -65°, the reaction mixture was allowed to warm to 0° (about five minutes was required to obtain this temperature) and was then stirred at 0° for exactly one hour. After carbonation of the reaction mixture and isolation of products in the manner described for the previous reaction with lithium, there was obtained 2.95 g. of neutral material and 5.05

g. of acidic material. The acidic material after sublimation at 0.05 mm. at a bath temperature of 200-210° amounted to 4.56 g. (55 per cent yield) of acid, m.p. 183-186°. A second sublimation gave 4.36 g. of acid of the same m.p. A portion of this acid (2.00 g.) after recrystallization from benzene gave 1.85 g. of crystals, m.p. 186.1-187.1°.

Anal. Found: C, 83.28, 83.37; H, 6.15, 6.26. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37.

This acid gave no depression of m.p. when mixed with an authentic sample of 2,2,4-triphenylbutanoic acid (synthesized by the procedure given previously), while a 50/50 mixture with 3,3,4-triphenylbutanoic acid melted at 148-162°. The infrared spectrum of this acid (either after the first sublimation or after recrystallization) was identical with that of the authentic sample of 2,2,4-triphenylbutanoic acid.

In another run a small portion of a solution of 10.0 g. (32.6 mmoles) of 1-chloro-2,2,3-triphenylpropane in 25 ml. of tetrahydrofuran was added to 0.70 g. (0.997 g. atom) of lithium in 250 ml. of tetrahydrofuran. When after 30 minutes of vigorous stirring at -10° no evidence of reaction was observed, 0.6 ml. of methyl iodide was added and a red color appeared after 20 minutes of additional stirring. The reaction temperature was lowered to -65 ±5° and the remainder (at least 95 per cent) of the chloride was added over a period of 30 minutes. Stirring was continued for an additional three hours at -65°. The reaction mixture was then allowed to warm with stirring to 0° (five minutes was required to attain this temperature) and stirred at 0° for 15 minutes before carbonation. After the usual isolation procedure, there was obtained 4.29 g. of neutral material and 4.58 g. of acidic material. The acidic material after

sublimation at 0.09 mm. at a bath temperature of 200-210° amounted to 4.20 g. (41 per cent yield) of acid, m.p. 177-185°. After two additional sublimations 3.98 g. of acid, m.p. 182-187°, was obtained. The infrared spectrum of this acid was essentially identical with that of an authentic sample of 2,2,4-triphenylbutanoic acid. A finely ground mixture of 5 per cent 3,3,4-triphenylbutanoic acid and 95 per cent 2,2,4-triphenylbutanoic acid melted at 165-184° and after resolidification melted at about 172-184°; therefore, it appears likely that the acid of m.p. 182-187° consisted of 2,2,4-triphenylbutanoic acid with less than 2 mole per cent impurity. A portion (2.00 g.) of the acid of m.p. 182-187° was recrystallized from benzene and then sublimed in vacuo to give 1.80 g. of acid, m.p. 186.1-187.1°. This acid gave no depression when mixed with an authentic sample of 2,2,4-triphenylbutanoic acid.

Reactions of 1-Chloro-2-methyl-2-phenylpropane (Neophyl Chloride)

2-Methyl-2-phenylpentanone-4.--This ketone was prepared by the method of A. Hoffman.[41] In a 500 ml. erlenmeyer flask equipped with water bath and magnetic stirrer was placed 90.0 g. (0.67 mole) of anhydrous granular aluminum chloride and 200 ml. (2.24 moles) of dry thiophene-free benzene. This mixture was stirred while 50.0 g. (0.51 mole) of mesityl oxide was added dropwise over a period of one hour. The stirring was then continued for another four hours. The mixture was poured onto ice and the water separated, dried over anhydrous calcium sulfate and filtered. It was then distilled at reduced pressure to give 48.0 g. (53.4 per cent yield) of product of b.p. 105° at 8 mm.

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(41) A. Hoffman, J. Am. Chem. Soc., 51, 2542 (1929).

3-Methyl-3-phenylbutanoic Acid.--The preparation of this acid was attempted by the method of A. Hoffman.[41] This procedure consisted of treatment of 2-methyl-2-phenylpentanone-4 with sodium hypobromite solution; however, this procedure failed to give any of the desired acid. The ketone was successfully oxidized to the acid with a solution of potassium hypochlorite solution prepared according to the procedure given in Organic Syntheses.[42] A solution of 0.58 mole of potassium hypochlorite and 10.0 g. (0.057 mole) of 2-methyl-2-phenylpentanone-4 was stirred at reflux for 24 hours. At this time the reaction mixture was tested for hypochlorite ion (with a solution of NaI, HOAc and starch) with negative results. Another 0.58 mole of potassium hypochlorite was added and the mixture stirred at reflux for an additional 23 hours at which time it gave a positive test for hypochlorite ion. The excess potassium hypochlorite was destroyed with sodium bisulfite and the neutral oil was extracted with ether. The aqueous layer was acidified and extracted with ether. The ether solution was dried over anhydrous magnesium sulfate and filtered, and then the ether was removed by distillation. The remaining oil was distilled at 100-135° at 0.20 mm. and a clear liquid was obtained which solidified to give 6.1 g. (60.5 per cent yield) of soft white crystals. This 6.1 g. of acid was sublimed at 70-90° and a pressure of 150 microns to give 4.33 g. of soft crystals which were recrystallized from n-pentane to give 3.22 g. with m.p. 46-57°. Two more sublimations and two more recrystallizations from n-pentane gave 2.05 g. of acid with m.p. 56.0-58.0°, reported[41] m.p. 57.5-58.5°.

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(42) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 429.

2-Methyl-2-phenylbutanoic Acid.--A Grignard reaction was employed to prepare 2-phenyl-2-butanol from ethyl bromide and acetophenone. The alcohol was converted to 2-phenyl-2-butanol methyl ether by the method of Wallis and Bowman.[43] Treating 58 g. (0.39 mole) of 2-phenyl-2-butanol in 100 ml. (2.48 moles) of methyl alcohol with 3.6 ml. of concentrated sulfuric acid and allowing to stand overnight gave 39 g. (61.5 per cent yield) of 2-phenyl-2-butanol methyl ether. This ether was converted to 2-methyl-2-phenylbutanoic acid by a procedure similar to that used by Wallis and Bowman. Finely divided sodium-potassium alloy was prepared with the Morton stirrer from 8.0 g. (0.20 g. atom) of potassium and 1.0 g. (0.043 g. atom) of sodium in 250 ml. of tetrahydrofuran. Twenty grams (0.12 mole) of the ether was added dropwise over a period of 30 minutes at room temperature with rapid stirring. A red color was noted immediately upon addition of the first few drops of the ether. After stirring an additional 10 minutes the stirring had to be stopped because of agglomeration of the remaining sodium-potassium alloy. The reaction mixture was allowed to stand for 2-1/2 hours and then forced onto solid carbon dioxide. The reaction mixture was made slightly acidic with hydrochloric acid and the solvent removed on the steam bath. The residue was treated with an excess of aqueous sodium hydroxide and extracted with ether. The ether extract contained 3.27 g. of neutral material. Acidification of the aqueous solution and extraction with ether gave 9.77 g. (45.5 per cent yield) of crude acid. Two sublimations and a recrystallization from n-pentane gave 4.71 g. of white crystals of m.p. 57.0-58.0°, reported[43] m.p. 57-58°.

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(43) E. S. Wallis and P. I. Bowman, J. Org. Chem., 1, 383 (1936).

2,2-Dimethyl-3-phenylpropanoic Acid.--A Grignard reaction[44] between benzyl chloride and acetone was used to prepare 2-benzyl-2-propanol in 70 per cent yield. The alcohol was converted to the chloride by the procedure of Brown and Fletcher.[45] A mixture of 167 g. (1.11 moles) of the alcohol and 456 ml. (5.45 moles) of concentrated hydrochloric acid was shaken for one hour in a separatory funnel. The aqueous layer was drawn off and replaced by 456 ml. of fresh concentrated hydrochloric acid and shaken for another hour. The upper layer was separated and dried over calcium chloride. Distillation, through a vacuum-jacketed column (1.5 cm. in diameter and 87 cm. in length) packed with glass helicies, yielded 128 g. (68.5 per cent yield) of 2-benzyl-2-chloropropane of b.p. 65-66° at 4 mm.

This chloride was then converted to the corresponding acid by means of a Grignard reaction. This represents a new method of preparing this acid. A solution of 84.2 g. (0.50 mole) of 2-benzyl-2-chloropropane in 200 ml. of ether was slowly added over a period of 1-1/2 hours to 12.5 g. (0.52 mole) of magnesium turnings, a crystal of iodine and 50 ml. of ether in the usual Morton apparatus. Stirring was continued for another 1/2 hour at which time the Grignard reagent was forced onto solid carbon dioxide. The reaction mixture was acidified with dilute hydrochloric acid and the organic material was extracted with four 100 ml. portions of ether. The resulting ether solution was extracted with four 100 ml. portions of aqueous sodium hydroxide. On acidification of the sodium hydroxide

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(44) V. Grignard, Comp. rend., 130, 1322 (1900).

(45) H. C. Brown and R. S. Fletcher, J. Am. Chem. Soc., 71, 1845 (1949).

solution, an oil separated which was taken up in ether and dried over magnesium sulfate. Removal of the ether yielded 9.0 g. (10 per cent yield) of white crystals, m.p. 53-57°. Two sublimations and one recrystallization from n-pentane gave 7.47 g. of 2,2-dimethyl-3-phenylpropanoic acid, m.p. 57.0-58.0°, reported[46] m.p. 56.5-58.0°.

Mixed melting points of 2,2-dimethyl-3-phenylpropanoic acid, 2-methyl-2-phenylbutanoic acid and 3-methyl-3-phenylbutanoic acid were taken. A 50-50 mixture of any two of the above three isomeric acids melted below room temperature.

2-Methyl-1-phenylpropane.--This hydrocarbon was prepared from 2-benzyl-2-chloropropane which had been prepared by the method given previously. A three-necked 300 ml. round-bottomed flask was fitted with condenser, dropping funnel, and magnetic stirrer. Fifty milliliters of dry ether 3.4 g. (0.14 mole) of magnesium turnings and a crystal of iodine was placed in the flask. A solution of 25 g. (0.14 mole) of 2-benzyl-2-chloropropane in 100 ml. of dry ether was added over a period of one hour. The mixture was stirred at reflux for 2-1/2 hours and then hydrolyzed with an aqueous ammonium chloride solution. The organic material was extracted with three 100 ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered and the ether was removed on the steam bath. Distillation of the residue gave 10.55 g. (53 per cent yield) of 2-methyl-1-phenylpropane, b.p. 158° at atmospheric pressure, reported[47] b.p. 171.4°. This product was analyzed by vapor-phase chromatography

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(46) A. Haller and E. Bauer, Compt. rend., 149, 5 (1909).

(47) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Thirty-second Edition, Cleveland, Ohio, 1950, p. 734.

(details given in a later section) and found to be 94 per cent pure.

2-Phenylbutane.--This hydrocarbon was prepared from 2-phenyl-2-butanol methyl ether that was prepared in the synthesis of 2-methyl-2-phenylbutanoic acid. Forty grams (0.24 mole) of the ether was cleaved with sodium-potassium alloy, 2 g. (.086 g. atom) sodium and 16 g. (0.41 g. atom) potassium, in the manner described in the synthesis of 2-methyl-2-phenylbutanoic acid. After the ether was reacted with the sodium-potassium alloy, t-butyl alcohol was added and then ethanol until all of the excess sodium-potassium alloy was consumed. The resulting mixture was acidified and the solvents removed on the steam bath. Several hundred milliliters of water was added to the residue and the resulting mixture was extracted with three 125 ml. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and filtered. The ether was removed on the steam bath. Initial attempts to distill the residue failed because of extensive frothing. The residue was flash distilled in a Claisen flask fitted with dropping funnel, thermometer, condenser and receiver. The residue was added dropwise to the Claisen flask which was heated by an oil bath maintained at 250°. The residue distilled at an indicated 150-160°. The distillate was redistilled through an electrically heated vigreux column (1.0 cm. in diameter and 25 cm. in length) and gave 11.0 g. (33.6 per cent yield) of 2-phenylbutane, b.p. 171.5° at atmospheric pressure, reported[48] b.p. 169-170°. This product was analyzed by vapor-phase chromatography and found to be 98 per cent pure.

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(48) H. Meyer and K. Bernhauer, Monatsh., 53/54, 721 (1929).

2-Methyl-2-phenylpropane.--Matheson white label grade was used without further purification. This material was analyzed by vapor-phase chromatography and found to be 100 per cent pure.

ortho-t-Butyltoluene.--This hydrocarbon was prepared by the method of Serijan and co-workers.[49] A solution of 513.0 g. (3.0 moles) of ortho-bromotoluene in 200 ml. of anhydrous ether was added to a stirred mixture of 80.2 g. (3.3 moles) of magnesium turnings in 500 ml. of anhydrous ether over a period of two hours. The resulting mixture was stirred for an additional 3-1/4 hours. Then a solution of 250.0 g. (2.7 moles) of t-butyl chloride in 200 ml. of ether was added with stirring over a period of 45 minutes. The mixture was then stirred for an additional 6 hours. At this time, the mixture had become so thick and viscous that stirring was no longer effective so stirring was stopped and the mixture was allowed to stand for ten hours. The mixture was then hydrolyzed with dilute hydrochloric acid and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and filtered. Removal of the ether on the steam bath and distillation of the residue through an electrically heated column (1.6 cm. in diameter and 34 cm. in length) packed with glass helices gave 48.4 g. (12 per cent yield) of ortho-t-butyltoluene, b.p. 194-197° at atmospheric pressure, reported[49] b.p. 200.4°.

ortho-t-Butylbenzoic Acid.--This acid was prepared by oxidizing ortho-t-butyltoluene by the procedure given by Shriner and Fuson.[50] A mixture of

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(49) K. T. Serijan, H. F. Hipsher and L. C. Gibbons, J. Am. Chem. Soc., 71, 873 (1949).

(50) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Second Edition, J. Wiley and Sons, Inc., New York, N. Y., 1940, p. 164.

20.0 g. of ortho-t-butyltoluene, 80.0 g. of potassium permanganate, 2.0 g. of sodium hydroxide and 1200 ml. of water was placed in a 3 l. erlenmeyer flask. The flask was equipped with reflux condenser and magnetic stirrer and was stirred at reflux for 18 hours, at which time the permanganate color was gone. The solution was filtered to remove the manganese dioxide and extracted with ether to remove neutral impurities. The basic solution was acidified and extracted with ether. The ether extract yielded 17.1 g. of an acidic oil. Vacuum distillation gave 12.8 g. of oil, b.p. 136-138° at 1 mm. pressure. This oil was crystallized from n-pentane and gave 11.0 g. of white crystals, m.p. 57-60°. Another recrystallication from n-pentane gave 9.85 g., m.p. 60-63° and a recrystallization from methylene chloride gave 7.42 g., m.p. 60-63°. This 7.42 g. was chromatographed using silicic acid and chloroform and yielded, after a recrystallization from n-pentane, 5.11 g., m.p. 61-66°. Another recrystallization from n-pentane, followed by vacuum sublimation at 60 microns and a bath temperature of 55° gave 3.88 g., m.p. 64-68°. Another sublimation, discarding a small amount of the first material to sublime, gave 2.49 g., m.p. 67-69°, reported[49,51,52] m.p. 80.3-80.8°, 68.5°, 70°.

A 0.80 g. sample of the above acid was nitrated according to the procedure of Crawford.[51] The acid was added to 10 ml. of concentrated HNO_3 and heated on the steam bath for 2-1/2 hours. The resulting mixture was poured onto ice, filtered, and recrystallized twice from benzene yielding 0.46 g. of 2-t-butyl-5-nitrobenzoic acid, m.p. 169.0-170.5°, reported[51] m.p. 170°.

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(51) M. Crawford and F. H. C. Stewart, J. Chem. Soc., 4443 (1952).

(52) K. Alder, K. Heimback and E. Kuhle, Chem. Ber., 1364 (1953).

meta-t-Butyltoluene.--This hydrocarbon was prepared from m-bromotoluene. The meta-bromotoluene was obtained from the undergraduate organic laboratory where it is regularly prepared by the students. It was redistilled through an electrically-heated column (1.6 cm. in diameter and 34 cm. in length) packed with glass helices and was collected at 179-181°, reported[53] b.p. 183.7°. A 513.0 g. portion of the above halide was subjected to the same procedure used in the preparation of ortho-t-butyltoluene and yielded 38.6 g. (9.6 per cent yield) of meta-t-butyltoluene, b.p. 184-185°, reported[49] b.p. 189.3°.

meta-t-Butylbenzoic Acid.--Twenty grams of meta-t-butyltoluene was oxidized by the procedure given in the preparation of ortho-t-butylbenzoic acid and gave 16.0 g. of white crystals m.p. 120-124°. Four recrystallizations from aqueous alcohol gave 7.60 g. of acid, m.p. 127-128°, reported[49] m.p. 127.0-127.6°.

para-t-Butylbenzoic Acid.--Twenty grams of para-t-butylbenzoic acid (Eastman practical grade) was twice recrystallized from 95 per cent ethanol and yielded 12.0 g. of acid, m.p. 164.0-165.0°, reported[49] m.p. 165.0-165.6°.

1-Chloro-2-methyl-2-phenylpropane (Neophyl Chloride).--This compound was prepared by the method of Whitmore and co-workers.[54] A mixture of 1050 g. (13.5 moles) of dry thiophene-free benzene and 75 g. (0.72 mole) of concentrated sulfuric acid was placed in a 3.1 Morton flask and stirred vigorously at 20° while 450 g. (4.98 moles) of methallyl chloride was added

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(53) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Thirty-second Edition, Cleveland, Ohio, 1950, p. 1144.

(54) F. C. Whitmore, C. A. Weisgerber and A. C. Shabica, Jr., J. Am. Chem. Soc., 65, 1469 (1943).

dropwise over a period of seven hours. Stirring at room temperature was then continued for another four hours. The benzene solution was separated from the sulfuric acid and washed with aqueous sodium bicarbonate and then with several portions of water. The excess benzene was removed on the steam bath and the remaining liquid was dried overnight over sodium sulfate. The liquid was filtered and distilled through a vacuum-jacketed column (1.5 cm. in diameter and 87 cm. in length) packed with glass helices. The halide was collected at 96° and 13 mm. pressure (reported 97° at 13 mm.) and yielded 594 g. (70.7 per cent yield), $n_D^{23} = 1.5236$, reported[54] $n_D^{20} = 1.5250$.

Reaction of Neophyl Chloride with Sodium in Dioxane--t-Amyl Alcohol.--This reaction was carried out by the procedure of Grovenstein.[6] In the usual Morton apparatus was placed 30 g. (0.18 mole) of neophyl chloride, 15.9 g. (0.68 g. atom) of sodium, 280 ml. (2.56 moles) of dry t-amyl alcohol and 220 ml. of dioxane. The resulting mixture was heated to reflux and slowly stirred at reflux for one hour until the initial exothermic reaction slowed. The mixture was then stirred vigorously at reflux for another hour. Next 50 ml. of ethanol was added to destroy the remaining sodium. The mixture was then acidified and concentrated to about 100 ml., an equal volume of water added, and the mixture extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate, filtered and the ether was removed on the steam bath. The residue was distilled through a vigreux column (1.5 cm. in diameter and 12 cm. in length) and 12.0 g. of liquid of indicated b.p. 145-155° (obviously inaccurate because thermometer bulb too high in still head) collected while 1.5 g. of non-distilled residue remained in distilling flask. The above 12.0

g. of liquid was redistilled through a column (1.6 cm. in diameter and 34 cm. in length) packed with glass helices to give 10.34 g. (43.5 per cent yield) of hydrocarbon of b.p. 167° and 0.8 g. of non-distilled residue remaining in the distilling flask. Since the combined distillate and residue from the initial distillation were only 13.5 g. and the theoretical yield of hydrocarbon was 23.8 g., it would appear that an error was made in some of the weighings in this experiment. The above 10.34 g. of hydrocarbon was analyzed by vapor-phase chromatography (details given in following section) and found to contain 98.3 per cent 2-methyl-2-phenylpropane and 1.7 per cent 2-phenylbutane and/or 2-methyl-1-phenylpropane.

Reaction of Neophyl Chloride with Lithium in Tetrahydrofuran at -65° for 3-1/2 hours.--In the usual apparatus for alkali metal reactions was placed 250 ml. of tetrahydrofuran and 1.05 g. (0.15 g. atom) of chopped lithium tape. The protective paraffin coating on the lithium tape was removed with dry benzene and the excess benzene removed by blotting the tape with a paper towel. The reaction was initiated at -10° by adding a small amount (ca. 5%) of a solution of 10.0 g. (0.059 mole) of neophyl chloride in 25 ml. of tetrahydrofuran and 0.6 ml. of methyl iodide. As soon as the reaction was initiated, the temperature was lowered to -65° and the remaining halide solution was added over a period of 30 minutes. The solution was yellow in color and stirring was continued for 3-1/2 hours at -65°. The reaction mixture was forced onto pulverized solid carbon dioxide and allowed to stand overnight. The next day the reaction mixture was acidified with 10 per cent hydrochloric acid, which reacted with the remainder of the lithium, and the solvents were removed in vacuo at steam

bath temperature. The residue was treated with an excess of aqueous sodium hydroxide and 2.38 g. of neutral material was extracted with ether. Acidification and extraction with ether gave, in the ether extract, 7.45 g. of acidic material. The acidic material obtained was pink in color apparently due to iodine, so it was dissolved in ether and the ether solution extracted with a sodium thiosulfate solution (100 ml. of H_2O, 2 g. of $Na_2S_2O_3$, 1 g. NaI and 1 ml. HOAc). On removing the ether 6.95 g. of white crystals, m.p. 53-58°, was obtained. This 6.95 g. of acid was sublimed at 65-70° at 40 microns and gave 6.40 g. of acid, m.p. 56.5-58.0°. A 2.0 g. sample of this was recrystallized to give 1.87 g., m.p. 56.5-58.0°. A mixed melting point of this acid and authentic 3-methyl-3-phenylbutanoic acid (m.p. 56.0-58.0°) gave no depression. However, mixed melting points of this acid with 2-methyl-2-phenylbutanoic acid (m.p. 57.0-58.0°) and with 2,2-dimethyl-3-phenylpropanoic acid (m.p. 57.0-58.0°) both gave large depressions (i.e., the 50/50 mixture was molten at room temperature).

Reaction of Neophyl Chloride with Lithium in Tetrahydrofuran at -65° for 3 hours then 30° for four hours.--The same procedure and quantity of reactants as in the previous reaction with lithium was used up to the end of the period of stirring at -65° for 3 hours. The reaction mixture was then warmed to 30° and stirred at this temperature for 4 hours. After carbonation of the reaction mixture and isolation of products in the manner described for the previous reaction with lithium, there was obtained 2.05 g. of neutral material, 0.91 g. of acidic ether-soluble material and 0.71 g. of a black, tarry, acidic, ether-insoluble material. Much of the neutral material was apparently lost by volatilization while removing the solvents

in vacuo on the steam bath. The 0.91 g. of acidic material was distilled at 160° at 80 microns and gave 0.40 g. of yellow oil. The infrared spectrum of this material was similar but not identical to those of 3-methyl-3-phenylbutanoic acid, 2-methyl-2-phenylbutanoic acid or 2,2-dimethyl-3-phenylpropanoic acid. The above 0.40 g. of acidic material was esterified with diazomethane and analyzed by vapor-phase chromatography (details given in following section). This chromatography showed that the acidic material contained none of the following acids: 3-methyl-3-phenylbutanoic acid, 2-methyl-2-phenylbutanoic acid, 2,2-dimethyl-3-phenylpropanoic acid, ortho-, meta-, and para-t-butylbenzoic acids. The above methylated acidic material gave a positive test for unsaturation with potassium permanganate solution, but the further characterization of this material was not attempted because it was isolated in such small yield.

Reaction of Neophyl Chloride with Lithium in Tetrahydrofuran at -65° for 3 hours then 0° for 1 hour.--The same procedure as in the previous reaction with lithium was used up to the end of the period of stirring at -65° for 3 hours. The reaction mixture was then warmed to 0° and stirred at this temperature for one hour and then forced onto dry ice. After accidification, the solvents were carefully removed on the steam bath at atmospheric pressure to prevent loss of neutral material. The extraction procedure used in the previous reactions gave 6.72 g. of neutral material and 3.53 g. of acidic material. The acidic material was distilled at 95-145° at 80 microns and gave 2.88 g. of soft yellow crystals. This material was sublimed at 50° at 80 microns giving 2.63 g. of white crystals, m.p. 41-54°. The infrared spectrum of this material shows characteristic absorption maxima near 7.62 and 13.3 microns. The infrared spectrum of

3-methyl-3-phenylbutanoic acid shows these same absorption maxima at 7.62 and 13.13 microns. In contrast, 2-methyl-2-phenylbutanoic acid has characteristic absorption maxima at 8.62, 9.95, and 13.80 microns and 2,2-dimethyl-3-phenylpropanoic acid has absorption maxima at 8.62 and 13.64 microns. Comparison of these spectra show that this acid isolated from this reaction is predominantly 3-methyl-3-phenylbutanoic acid. The neutral material was distilled at 50-100° at 22 mm. pressure and gave 5.21 g. of distillate. The infrared spectrum of this material had characteristic absorption maxima at 7.90, 8.34 and 8.94 microns. The infrared spectrum of t-butylbenzene had these same maxima at almost equal intensity indicating that t-butylbenzene was the major component of the neutral material. The starting halide had characteristic absorption maxima at 7.80 and 14.07 microns. The above 5.21 g. of neutral distillate was analyzed by vapor-phase chromatography and found to contain 58.2 per cent 2-methyl-2-phenylpropane and 8.4 per cent 2-phenylbutane and/or 2-methyl-1-phenylpropane. Esterification and vapor-phase chromatography of the above 2.63 g. of acidic material showed it contained 98.3 per cent 3-methyl-3-phenylbutanoic acid and 2.5 per cent ortho-t-butylbenzoic acid.

Reaction of Neophyl Chloride with Lithium in Tetrahydrofuran at -65° for 3 hours then 0° for 1 hour with Na-K Alloy added.--The same procedure as in the previous reactions with lithium was used up to the end of the period of stirring at -65° for 3 hours. The reaction mixture was then warmed to 0°, Na-K alloy (10.5 g. potassium and 2.6 g. sodium) was added and the mixture was stirred vigorously at 0° for one hour and then forced onto solid carbon dioxide. The resulting mixture was acidified and the solvents removed on the steam bath at atmospheric pressure. The extraction procedure

used in the previous reactions with lithium gave 5.44 g. of neutral material and 4.33 g. of acidic material. The acidic material was distilled at 105-120° at 80 microns. During the distillation the distillate became deep purple apparently due to a small amount of iodine being liberated. Treatment with sodium thiosulfate solution removed the color and gave 2.60 g. of a clear colorless oil. This was redistilled at 85-104° at 70 microns pressure and gave 1.80 g. of a pink oil which darkened on standing. After letting stand for one week in the sunlight, the oil was decolorized with sodium thiosulfate solution and distilled at 75-85° at 50 microns pressure giving 1.65 g. of soft white crystals, m.p. 49-56°. The infrared spectrum of these crystals was almost identical to the spectrum of the acid produced in the preceding experiment and the same interpretation indicates that this material is predominantly 3-methyl-3-phenylbutanoic acid. The above 1.65 g. of acidic material was esterified and subjected to vapor-phase chromatography. The acidic material contained 88.0 per cent 3-methyl-3-phenylbutanoic acid and 2.4 per cent ortho-t-butylbenzoic acid. The above 5.44 g. of neutral material was analyzed by vapor-phase chromatography and found to contain 30.2 per cent 2-methyl-2-phenylpropane and 4.9 per cent 2-phenylbutane and/or 2-methyl-1-phenylpropane.

Analyses by Vapor-phase Chromatography.--A Perkin-Elmer Vapor Fractometer Model 154D was utilized for these analyses. The neutral material resulting in the reactions (described previously) of 1-chloro-2-methyl-2-phenylpropane with sodium and t-amyl alcohol and with lithium was analyzed for 2-methyl-2-phenylpropane, 2-phenylbutane, and 2-methyl-1-phenylpropane. No conditions could be found which would separate all three of the above

hydrocarbons, but 2-methyl-2-phenylpropane could be separated from 2-phenylbutane and 2-methyl-1-phenylpropane. The column giving the best separation and the one used for these analyses was one prepared by Jones.[55] This column consisted of a six-meter length of 1/4 in. O. D. copper tubing packed with unactivated Chromasorb supporting 20 per cent Dow-Corning High Vacuum Silicone Stopcock Grease by weight. The follcwing conditions were used in the quantitative analysis of the hydrocarbon mixtures: oven temperature 155°, 30 p.s.i. of helium gas, 31 rotometer reading, sensitivity 8, and 5 microliter samples. The peak areas were calculated by the method of multiplying peak height times peak width at 1/2 peak height. The results of these analyses are given in Table 2.

The acid material resulting in the reactions of 1-chloro-2-methyl-2-phenylpropane with lithium was analyzed for 3-methyl-3-phenylbutanoic acid, 2-methyl-2-phenylbutanoic acid, 2,2-dimethyl-3-dimethyl-3-phenyl-propanoic acid, ortho-, meta-, and para-t-butylbenzoic acids. The samples of acid material to be analyzed and pure samples of each of the above acids were methylated with diazomethane before the vapor-phase chromatography was done. The analyses were done on two different columns because no one column would separate all six esters. One of the columns was a Perkin-Elmer column O. This column was two meters in length, made of 1/4 in. O.D. stainless steel tubing packed with diatomaceous earth, supporting silicone grease. The following conditions were used with column O: oven temperature 147°, 20 p.s.i. of helium gas, 64 rotometer reading, sensitivity 4, and 5 microliter samples. The other column used

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(55) R. Jones, The Catalytic Hydrogenation of Some Tall Oil Constituents, Unpublished Ph. D. Thesis, Georgia Institute of Technology, 1961, p. 97.

was a Perkin-Elmer column P. This column was two meters in length, made of 1/4 in. O. D. stainless steel tubing packed with diethylene glycol. The following conditions were used with column P: oven temperature 163°, 20 p.s.i. of helium gas, 34 rotometer reading, sensitivity 4, and 5 microliter samples. The peak areas were calculated by the method of multiplying peak height times peak width at 1/2 peak height. The results of these analyses are given in Table 3. The peak areas were considered

Table 2. Analyses of Neutral Material Resulting from Reactions of 1-Chloro-2-methyl-2-phenylpropane with Alkali Metals

	Retention Time, min.	Peak Area	Per Cent
2-Methyl-2-phenylpropane	12.1	230.0	100.0
2-Phenylbutane	13.0	222.3	100.0
2-Methyl-1-phenylpropane	12.9	226.8	100.0
Neutral material from reaction of 1-chloro-2-methyl-2-phenylpropane with sodium and t-amyl alcohol*	12.1	222.4	98.3
	12.9	3.3	1.7
Neutral material from reaction of 1-chloro-2-methyl-2-phenylpropane with lithium for 3 hrs. at -65°, then 1 hr. at 0°*	12.1	132.0	58.2
	12.9	19.0	8.4
	14.1	10.4	4.6
	16.9	12.2	5.4
	17.8	13.0	5.7
Neutral material from reaction of 1-chloro-2-methyl-2-phenylpropane with lithium for 3 hrs. at -65°, then 1 hr. with NaK at 0°**	12.1	68.5	30.2
	12.9	11.0	4.9

*Samples distilled before analysis.

**Solvents removed by distillation in vacuo and part of neutral material lost by volatilization.

Table 3. Analyses of Acidic Material* Resulting from Reactions of 1-Chloro-2-methyl-2-phenylpropane with Lithium

	Column P			Column O		
	Retention Time, min.	Peak Area	Per Cent	Retention Time, Min.	Peak Area	Per Cent
2,2-Dimethyl-3-phenylpropanoic acid	12.0	458	100.0	8.3	354	100.0
2-Methyl-2-phenylbutanoic acid	13.4	472	100.0	8.8	344	100.0
ortho-t-Butylbenzoic acid	14.6	480	100.0	9.1	342	100.0
meta-t-Butylbenzoic acid	14.9	503	100.0	11.2	381	100.0
3-Methyl-3-phenylbutanoic acid	17.1	455	100.0	9.2	336	100.0
para-t-Butylbenzoic acid	19.0	500	100.0	13.5	376	100.0
Acidic material from reaction of 1-chloro-2-methyl-2-phenylpropane with lithium for 3 hrs. at -65°, then 1 hr. at 0°**	14.4	11	2.3	9.2	332	98.8
	17.0	447	98.3			
	26.0	12	2.5	12.8	12	3.2
Acidic material from reaction of 1-chloro-2-methyl-2-phenylpropane with lithium for 3 hrs. at -65°, then 1 hr. with Na-K at 0°**	10.0	6	1.3	7.4	5	1.5
	14.4	11	2.4			
	17.0	389	88.0	9.2	292	86.9
	20.2	18	3.8	11.8	14	4.1
				17.2	12	3.5
Acidic material from reaction of 1-chloro-2-methyl-2-phenylpropane with lithium for 3 hrs. at -65°, then 4 hrs. at 30°**	16.2	150	31.5	8.3	103	29.0
	26.0	138	29.0	12.6	105	29.6
	35.7	28	5.9	15.4	11	3.2

*Acidic material was methylated with diazomethane before analysis.

**Acidic material was sublimed or distilled before methylation and analysis.

to be directly proportional to per cent of each component. The peak area of a five microliter sample of each reference compound was considered 100 per cent. The per cent of the unidentified peaks was calculated by considering them to be isomers of the reference compounds with 100 per cent being equal to the average peak area of the reference compounds.

CHAPTER IV

RECOMMENDATIONS

Since the rearrangement of 2,2,3-triphenylpropyllithium could be explained by an elimination addition mechanism, this possibility should be investigated. This mechanism requires benzyllithium and triphenylethylene as intermediates and if the reaction was run in the presence of one of these compounds which had been labeled with C^{14} it should lead to incorporation of the labeled molecules in the rearranged product. An absence of incorporation of the labeled molecules in the product would lend additional support to the carbanion mechanism.

It would also be of interest to attempt to identify some of the unknown neutral products in the reaction of neophyl chloride with lithium. Some likely possibilities would include 1-methyl-1-phenylcyclopropane, 1,2-dimethyl-1-phenylethylene and 1,1-dimethyl-2-phenylethylene. An attempt should be made to identify some of the unknown acidic products. A positive test for unsaturation indicates the presence of some unsaturated acids and the longer retention times in the vapor-phase chromatography suggests the possibility of some dibasic acids. Since the 2-methyl-2-phenylpropyllithium is protonated by tetrahydrofuran much faster than it rearranges, this reaction should be studied in less reactive solvents such as diethyl ether or benzene.

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